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Land Treatability of Refinery and Petrochemical Sludges

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16. ABSTRACT

The land disposal of API separator sludges was investigated with regard to decomposition rates of organic constitutents and the possible impact of these materials on plants and surface water or groundwater quality. Two oily sludges (one from a petroleum refinery and one from a petrochemical plant) were studied as to their phytotoxicity, biodegradability in soils, water-soluble constituents, and field mobility.

Concentrations of refinery sludge of 5% v/v and above depressed ryegrass emergence and yield. The petrochemical sludge suppressed emergence and yield proportional to the amount of sludge applied, and the suppression lasted longer than that of the refinery sludge.

Biodegradation rates were greatest when small applications of sludge were made at frequent intervals. Optimum application rates for both wastes was 5% to 10% (wt/wt).

The water-soluble compounds in both sludges were low indegradability, potentially toxic, and extremely mobile in high concentrations. These results indicate a need for careful management of land treatment sites to avoid groundwater contamination. Gas-liquid chromatography (GLC) combined with column chromatography is recommended for effective monitoring of oily wastes applied to soils.

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LAND TREATABILITY OF REFINERY AND PETROCHEMICAL SLUDGES

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and J.C. Thomas
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College Station, Texas 77843

Grant No. R 805474013

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that neccessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, soil, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

This report describes an evaluation of the fate, mobility, and potential environmental impact of the land treatment of two sludges which are commonly disposed of by land treatment.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

ABSTRACT

The land disposal of American Petroleum Institute separator sludges was investigated with regard to decomposition rates of organic constituents and the possible impact of these materials on plants and surface water or groundwater quality. Two oily sludges (one from a petroleum refinery and one from a petrochemical plant) were studied as to their phytotoxicity, biodegradability in soils, water-soluble constituents, and field mobility.

Concentrations of refinery sludge of 5% v/v (9 x 10^4 kg/ha) and above depressed ryegrass emergence and yield. The petrochemical sludge suppressed emergence and yield proportional to the amount of sludge applied, and the suppression lasted longer than that of the refinery sludge.

Biodegradation rates were greatest when small applications of sludge were made at frequent intervals. Optimum application rates for both wastes was 5% to 10% (wt/wt).

The water-soluble compounds in both sludges were low in degradability, potentially toxic, and extremely mobile in high concentrations. These results indicate a need for careful management of land treatment sites to avoid groundwater contamination. Lysimeter studies indicated greater mobility of organic waste constituents in coarse textured soils, but when the soils were not overloaded, the leachate water collected 150 cm below the surface was essentially free from contamination.

This report was submitted in fulfillment of Grant No. R 805474013 by the Texas Agricultural Experiment Station under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period October 10, 1977 to March 30, 1982, and work was completed as of July 30, 1982.

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SECTION 1

INTRODUCTION

Industrial activities produce many complex wastes that require disposal by economically and environmentally sound means. Oily wastes are often separated from reusable constituents or more easily disposed of materials by the use of API separators at petrochemical plants and depots. Certain fractions of the materials accumulate as sludge in these pits and must be periodically dredged or pumped out.

Disposal Practices

Past and current disposal technology has been listed to include landfilling, land treatment, surface impoundment, incineration, deep well injection, chemical fixation (Phung and Ross, 1978), and ocean dumping. A comparison of disposal methods by Grove (1978) concluded that for oily wastes, land treatment is generally the best method, combining degradation of the waste with low to moderate cost. Landfilling was shown to be less expensive, but the oil would not degrade and would prove to be a continuing pollution hazard while the land could not be reclaimed for other uses. Costs of landfilling have increased sharply since 1978 (unpublished data), thus making landfilling a less attractive option. Alternatively, incineration would degrade the waste, but stack emissions standards, which call for scrubbers and precipitators, and high energy consumption (Francke and Clark, 1974; Grove, 1978) may rule out incineration as too costly an option for some waste streams. Although Phung and Ross (1978) stated that landfilling is the most common current disposal practice for oily waste, Grove (1978) cited an EPA sponsored study which estimated that land treatment could grow in use from 7% of refinery sludges in 1976 to 34% by 1980.

Uses of Land Treatment

Land treatment, also called landfarming, landspreading, and soil incorporation, is the controlled disposal of waste on the soil surface accompanied by the continued monitoring and management of the disposal site. The technique of land treatment is not new; one refinery has practiced the land treatment of API separator sludges at one location since 1954. Currently, all of this company's domestic refineries as well as several of their overseas refineries, use this technique (I. Trotter, personal communication). Huddleston and Meyers (1978), Snyder _et al_. (1976), and Weldon (1978) have also reported on current operations in land treatment of refinery oily wastes. Other wastes, such as used oil and coolant (Francke and Clark, 1974) and oil spill debris (Stearns _et al_., 1977a), have also been successfully treated by incorporation into the soil.

DEGRADATION OF OILY WASTES IN SOILS

The ultimate fate of petroleum waste sludges applied to soils would ideally be their decomposition into water, carbon dioxide, and soil humus material. However, the likelihood exists that certain waste components or their degradation products could contaminate adjacent air, surface water, and groundwater. Although extensive monitoring and testing of operational land treatment sites have only begun in recent years, numerous laboratory studies have yielded a fairly clear understanding of the behavior of petroleum products and wastes in soils. Microbiological investigations have provided information on the factors influencing oil degradation rates, the common strains of oil degrading microbes, and the degradability of petroleum compounds. However, work concerning petroleum leaching, volatilization, and runoff has generally consisted of land treatment monitoring. Such monitoring activities have been minimal, and land treatment has often proceeded without documentation of runoff and leachate quality.

Microbial Species

Dobson and Wilson (1964) and Plice (1948) have shown that degradation of oil in soils is primarily biological. Increased microbial activity in oil-contaminated soils observed by Gudin and Syratt (1975) and Raymond _et al_. (1976) also indicated that degradation is due to microbial action. Stone _et al_. (1942) and Harris (1976) further stated that oil decomposing bacteria are common in most soils, even when there has been no exposure to oil. Microbial counts by Cooper and Hedrick (1976), Kincannon (1972), and Snyder _et al_. (1976) all showed several strains of _Pseudomonas_ present in large numbers in oily soils. Other microbial genera include _Arthrobacter_, _Flavobacterium_, _Corynebacterium_ (Kincannon, 1972;

Snyder *et al.*, 1976), and *Alcaligenes* (Cooper and Hedrick, 1976; Snyder *et al.*, 1976). Different activities by four bacteria isolates as they are exposed to more refined hydrocarbons showed that oil degradability is a function of petroleum composition (Cooper and Hedrick, 1976).

Substrate Subsceptibility

Degradative processes attenuate leaching losses of mobile petroleum compounds according to the compounds' susceptibility to decomposition. Oils vary in their degradability, lightweights degrade more easily than heavy oils, and paraffins more easily than aromatics and naphthenic oils (Stone *et al.*, 1942). Raymond *et al.* (1976) found that polar compounds degrade more slowly. According to Schwendinger (1968), the order of hydrocarbon utilization by microbes, from greatest to least, is straight chain paraffins > branched paraffins = aromatics > asphalts (higher molecular weights). Gudin and Syratt (1975), studying n-paraffins, elucidated the order of degradation to be $n\text{-}C_{32} > n\text{-}C_{35} > n\text{-}C_{37}$. This stability of polar and aromatic fractions in soils is unfavorable to containment of contaminants near the surface because these same fractions also include the water soluble components which could be leachable.

Aeration Effects

Management of sludge disposal operations strives to maximize degradation rates with the intent of allowing the greatest use from a given land area while minimizing contaminant losses from the soil. Crop investigations as early as 1919 suggested that oil damage in soil was due to poor aeration-water relations rather than direct toxicity (Carr, 1919). Results of studies by Schwendinger (1968) and Giddens (1976) support the assertion that crops can withstand large amounts of oil without toxic effects, and Udo and Fayemi (1975) have stated that anaerobic and hydrostatic conditions are responsible for poor plant responses. Observed effects of oil on crops reflect microbiological conditions within the soil. Harris (1976) observed that most oil-decomposing organisms are active only on the oil phase boundaries so that the type of bacteria and waste and the soil water content have less influence on oil degradation than available oxygen. From these observations it is expected that optimum conditions for degradation, favoring smaller leaching losses, should include a well-aerated system. In fact, cultivated, thus aerated, soils have been shown to exhibit faster degradation of applied oils (Plice, 1948; Dobson and Wilson, 1964). Microbial degradation experiments by Kappeler and Wuhrmann (1978) have also demonstrated the necessity of oxygen for the decomposition of water soluble components of gas and oil.

Fertilizer Effects

The nutrient balance further affects deterioration of oil. For instance, petroleum sludges have a high C:N ratio which can serve to limit microbial respiration to well below its potential. Addition of nitrogen fertilizer to oily soil by Gudin and Syratt (1975) more than doubled respiration immediately after application. Because of the low nitrogen content of hydrocarbons, Harris (1976) found that this nutrient element is most limiting to oil degradation, followed in importance by phosphorus. Upon fertilization with N, P, and K, decomposition rates have been shown by Kincannon (1972) to increase by as much as 100%, from 8 to 16 kg m^{-3} mo^{-1}. Fertilized land treatment plots in Utah exhibited 80% degradation after 18 months compared to 55% for unfertilized plots (Snyder *et al.*, 1976). Work on spilled oil in northern climates by Cook and Westlake (1973) also confirmed the positive effect of adding nutrients for stimulating decomposition.

Other Considerations

Several other parameters, some of which are beyond operator control, affect the degree of success in land treatment systems. Waste loading rates should be carefully controlled to prevent anaerobic conditions. It has been found in one case that 10% or greater initial oil levels minimized decomposition (Kincannon, 1972). Waste degradation is also dependent on soil chemical and physical properties as well as local climatic conditions. Raymond *et al.* (1976) found degradation to be significantly different between the climatic regimes of Marcus Hook, Pennsylvania; Tulsa, Oklahoma; and Corpus Christi, Texas. It has additionally been suggested that bacterial seeding can improve response time to waste application (Schwendinger, 1968), but findings by Cook and Westlake (1973) question the effectiveness of such a technique. However, regardless of the management techniques and environmental inputs, there remains the potential for leaching of some components of such a heterogeneous mixture as petroleum wastes.

API separator sludges vary depending on the particular products manufactured by the plant or handled by the depot.

They also vary from time to time because of changes in the concentrations of constituents in catalytic reactors and resulting shifts in production allocations. Nevertheless, careful selection of a group of wastes should make it possible to delineate the primary considerations for land treatment of these wastes.

Though certain parameters such as metal content and nutrient and salt loading can be used to gauge application rates with present knowledge, a dearth of information exists on the rate of organic constituent decomposition and the possible impact of these materials on plants or on surface or groundwater quality.

This study was undertaken to investigate these considerations with the ultimate goal of providing information that can be used to design, manage, and monitor land treatment of API separator sludges and related wastes. Because of the complexity of the study, it was divided into four sections: phytotoxicity, biodegradation, water soluble constituents, and mobility under field conditions. Each division will be discussed individually in the following sections.

SECTION 2

CONCLUSIONS

1. Loading rates as high as 20% (3.6 x 10^5 kg/ha) of refinery sludge had no adverse impact on ryegrass emergence, while as little as 5% (9 x 10^4) of petrochemical sludge significantly decreased emergence. Emergence from successive plantings increased until reaching control levels.

2. Yield depressions from the first ryegrass harvest were proportional to the amount of sludge applied. Average yields at a given loading rate continued to be less than those from the controls for about 5 months; subsequently they increased to a level dependent on the amount of slowly degradable oily materials present.

3. Sludge-treated soils exhibited increased water adsorption times, which indicated impaired plant-soil water relations.

4. Biodegradation rates of both the refinery and petrochemical sludges depended on the soil to which they had been applied. At field capacity, maximum biodegradation occurred in the Norwood sandy clay, and the minimum occurred in the Bastrop sandy clay loam.

5. Biodegradation rates were not correlated with soil pH in the range studied (5.6 to 7.7).

6. Field capacity was the optimum moisture content for the degradation of the refinery sludge while the petrochemical sludge did not show an optimum moisture content. Both sludges appeared to have a broad range of moisture contents (including conditions both wetter and drier than field capacity) that had little influence on the rate of biodegradation.

Rates decreased when the soil moisture potential approached saturation and -1500 kPa.

7. The rate of CO_2 evolution of both sludges increased with application rates. Inhibitory mechanisms appeared to result in smaller increases in biodegradation per amount of sludge applied between the 5 and 10% application rates. Biodegradation of the soil-applied sludges increased through 30 C and decreased slightly at 40 C. The biodegradation rate at 10 C was about half of the maximum found at 30 C.

8. The rates of CO_2 evolution were similar for both wastes at the same application rates; but since the petrochemical waste contained almost six times more carbon than the refinery waste, the proportion of applied carbon respired was much less for the petrochemical waste.

9. Small, frequent applications of both wastes yielded higher respiration rates per unit applied than did a single equivalent application.

10. The petrochemical sludge that contained a C:N ratio of 380:1 exhibited the greatest degradation rate at a C:N ratio of 124:1. But the refinery sludge, which contained a C:N ratio of 78:1, showed the greatest increase in biodegradation rate when the C:N ratio was adjusted to 9:1. Additions of P and K either alone or with nitrogen did not greatly affect the rates of biodegradation of either waste. Field data confirmed increased biodegradation resulting from N fertilization.

11. The water soluble fraction (WSF) of the API oil-water separator sludge is predominantly composed of aromatic compounds, mostly mono- and diaromatics such as phenols and naphthalenes. Toxicity information is scarce, but indications are that these compounds may present some acute toxicity to soil organisms and a chronic carcinogenic hazard to humans. As a group, the compounds are not easily degradable by soil micro-organisms.

12. At high concentrations, the soluble constituents of either sludge may be extremely mobile in surface soils. The compounds tend to move on soil TLC plates as a group, with mobilities relative to water (R_F) of 1.0 for all except the higher-molecular-weight phthalates. The mobilities may have resulted from the application exceeding the adsorption capacities of the soil. Soil column leaching results were inconclusive because of confounding by the soluble soil organic matter.

13. Low concentrations of water soluble compounds of both refinery and petrochemical sludges could potentially

reach ground water if excessive applications were made on sandy soils. Ease of movement in the soils tested and the relative resistance to degradation of soluble compounds favors leaching losses from the soil surface. However, potential pollutants may be attenuated by degradation, and concentrations of some soluble compounds may be reduced by volatilization. Hydrodynamic dispersion may further spread and damp the distribution of any spiked solutes, so only fairly uniform, low concentrations would be expected to enter the water table if the adsorption capacities of the soil were exceeded.

14. Degradation of refinery and petrochemical sludges applied to soils in lysimeters was monitored by gas liquid chromatography (GLC) analysis of soil extracts. Under field conditions, degradation was greatest over the summer months, June to August, and continued over the winter months, December to February, at reduced rates. Soil temperatures at 6.4 cm were 25 to 30 C in summer and 5 to 10 C in the winter months.

15. GLC scans showed materials resolved as peaks to be more rapidly degraded than more complex, higher molecular weight materials chromatographed as an unresolved cone. Peaks represented primarily saturates and di- and tri-aromatics while the conical area was mainly composed of higher condensed polynuclear aromatics with molecular weights over 250 g/mole and carbon numbers in excess of 19.

16. While the majority of organics applied were degraded or retained within the zone of incorporation, measurable levels of organics (greater than 1 mg/kg) migrated below the zone of incorporation.

17. Characteristic profiles suggested that physical migration was a significant factor in transport mechanisms. Migration of organic constituents was enhanced over winter months corresponding to higher rainfall and greater soil moisture contents.

18. Mobility of organic constituents was greatest in the sandy loam textured Lakeland soil series and least in the clay textured Nacogdoches soil.

19. Textural discontinuities associated with clay pan soils retarded downward migration of sludge and nutrients. Organic constituents that migrated downward into subsurface horizons were degraded at a diminished rate.

20. Leachate samples collected 160 cm below the zone of

incorporation were free of detectable organic contaminants.

21. While this research provided data on the movement of two organic (primarily saturated hydrocarbons) wastes in soil, further research is needed on the fate and mobility of other types of wastes under other environmental conditions.

SECTION 3

RECOMMENDATIONS

1. Initially, applications of oily sludges should be kept to 5% v/v (9×10^4 kg/ha) or less until it is determined in the field or by other testing methods if vegetation can be established on soils treated at higher rates.

2. Laboratory tests should be used to evaluate factors influencing the biodegradation of a waste material applied to soil and to assess the ability of a specific soil and its associated microorganisms to degrade and retain the waste of interest. These tests should also be used to evaluate the optimum application rate, application frequency, and rate of addition of mineral nutrients. The use of both CO_2 monitoring and residual hydrocarbon extraction should provide a reasonable estimate of the true rate of waste decomposition.

3. Small, frequent applications of 1% (1.8×10^4 kg/ha) to 5% (9×10^4 kg/ha) of the wastes to the soils tested appeared to result in the most rapid rate of degradation. This translates to a hydrocarbon application rate of 0.5% (9×10^3 kg/ha) to 3% (5.4×10^4 kg/ha) Wastes that contain a large percentage of hydrocarbons which are not susceptible to microbial attack may require lower application rates to prevent an accumulation of toxic residues.

4. The application rate depends on the mean soil temperature and moisture content. The mean soil temperature should be greater than 15 C for maximum waste application rates. Waste application rates at lower temperatures should be regulated by a degradation rate that is determined at a lower temperature. Waste application should be ceased if the soil moisture content is substantially greater than field capacity.

5. The addition of nitrogen and phosphorus may be used to enhance waste degradation while the optimum C:N:P ratio

in a waste-soil mixture is in the range of 50:2:1; nutrient additions depend on waste characteristics and should be determined by laboratory testing for each waste stream and each receiving soil.

6. When excessive amounts of oily waste are land applied, the soil microbial population is reduced. This reduction slows the process of waste degradation and results in a build-up of hydrocarbons in the soil. Waste application rates should be regulated so that microbial inhibition does not result from the application of excessive amounts of toxic waste constituents. The effect of waste addition on the microbial population of the soil will depend on the ratio of readily available substrate to toxic waste constituents. In other words, the effect of toxic constituents will be reduced when large quantities of non-toxic readily available substrates are present.

7. These studies need to be expanded to include other wastes that contain organic constituents other than those found in the waste used in the present study. Candidate wastes include pesticide sludge, pharmaceutical waste, solvent reclaiming waste, and wood preserving waste.

8. These tests do not, nor were they designed to, demonstrate a reduction in the hazardous characteristics of the waste but do demonstrate the ability of the soil microbes to degrade specific waste constituents. Biological analysis would need to be included in future laboratory studies of this nature to demonstrate a reduction in hazardous characteristics.

9. Maintenance of a favorable nutrient balance is required for dissipation of waste hydrocarbons by means of land treatment. Frequent monitoring of carbon-to-water soluble nitrogen ratios is recommended.

10. Soils with textural discontinuities should be sought for disposal sites.

11. If deep, sandy soils are used for land treatment of hydrocarbon waste streams, they are best managed by low loading rates at more frequent intervals.

12. Application rates and frequencies require downward adjustments over the cooler winter months to offset diminished degradation rates.

13. A rest period for degradation of more recalcitrant, heavier-molecular-weight components should be incorporated

into the management scheme.

14. Analytical techniques developed from waste characterization should be used to monitor and assess field degrdation and management inputs required.

15. Further research is needed to better define the mechanisms of hydrocarbon migration within land treatment facilities.

16. Further research is needed to optimize loading rates relative to nutritive requirements and climatic variables. Research is needed to better identify the upper limit of application rates to avoid excessive migration.

SECTION 4

PHYTOTOXICITY STUDY

INTRODUCTION

Currently, land treatment is being used increasingly as an economical disposal option, especially for oily sludges from the petroleum and petrochemical industries. Many problems still remain, including a need for additional information on optimum soil and climatic conditions, application rates, and frequency of sludge applications.

A considerable amount of research has been carried out on the detrimental effects of crude oil and gas on soils and plants (Baldwin, 1922; Murphy, 1929; Schollenberger, 1930; Harper, 1939; Plice, 1948; Schwendinger, 1968; Garner, 1971; and Odu, 1972). On the other hand, some authors have reported crop enhancement as a result of oil application (Carr, 1919; Schollenberger, 1930; Harper, 1939; and Plice, 1948). The current status of work in this field indicates that asphaltic oils are slowest to decompose in the soil (Dibble and Bartha, 1979). Oil, when applied, often has an initial detrimental effect on plants which decreases as the oil decomposes and the residuals are incorporated into the soil organic matter. Once the oils decompose, the residual organic matter and biological organisms may improve soil physical conditions and act as plant nutrient sources resulting in improved productivity (Plice, 1948; Mackin, 1950; and Baker, 1970).

At the present time, little research has been conducted on the degradation and phytotoxicity of complex sludges resulting from refinery and petrochemical activities. These sludge materials not only contain the oily compounds normally found in crude oil but also contain various amounts of the end products of refinery or chemical plant operations and any products resulting from the mixing of these compounds. Various constituents are likely to have herbicidal influence on vegetation which is required for closure of a land treatment facility.

TABLE 1. PHYSICAL PROPERTIES OF SOIIS UTILIZED IN GREENHOUSE STUDY

Soil	Sand %	Silt %	Clay %	Texture USDA	Bulk Density (g cm-3)			Percent Water Retention (v/v)			CEC[a] Meq/100g	Carbon %	pH
					FC*	WP+	OD=	SAT‡	FC	WP			
Bastrop	60.3	10.0	29.7	SCL	1.49	1.67	1.76	37.0	30.4	10.9	27.4	1.0	6.9
Lakeland	81.1	4.5	14.4	SL	1.38	1.39	1.39	43.6	10.0	2.8	0.3	0.4	6.5
Nacogdoches	41.8	12.9	45.3	C	1.4						17.2	1.3	5.6
Norwood	48.2	15.2	36.6	SC	1.44	1.48	1.49	40.0	31.8	10.8	19.6	1.4	7.7

* FC = Field capacity

+ WP = Wilting point

= OD = Oven dry

‡ SAT= Saturated

[a] CEC= Cation exchange capacity

This research was thus conducted to determine the phytotoxic effects of two complex oil-water separator sludges and the persistence of such effects.

MATERIALS AND METHODS

Soils

Four diverse soils were employed to represent a range of potential disposal sites. The soils were Bastrop (Udic Paleustalf), Lakeland (Typic Quartzipsamment), Nacogdoches (Rhodic Paleudalf) and Norwood (Typic Udifluvent). The soil characteristics are given in Table 1.

Wastes

Two oil-water separator sludges were utilized: one from a refinery and one from a petrochemical plant (referred to as refinery sludge and petrochemical sludge, respectively). Laboratory analysis of the sludges revealed the components listed in Table 2. Water content was determined by

TABLE 2. CHARACTERISTICS OF THE TWO API PIT WASTE MATERIALS

	Refinery	Petrochemical
Density	1.22g cm^3	1.15g cm^3
Cd	3.3 ppm	4.5 ppm
Cr	51.0 ppm	134.2 ppm
Cu	227.7 ppm	35.8 ppm
Pb	14.1 ppm	20.9 ppm
Ni	14.1 ppm	924.4 ppm
Se	9.2 ppm	9.7 ppm
Na	1,734.8 ppm	1,252.4 ppm
Va	6.5 ppm	14.9 ppm
Zn	555.2 ppm	656.0 ppm
Percent H_2O	46.0 %	12.0 %
Pentane extractable	72.0 %	63.0 %
Benzene extractable	22.0 %	36.0 %
CH_3Cl_2 extractable	6.0 %	1.0 %
Residue	49.3 %	42.8 %
Ash	41.0 %	25.0 %
Sulfur	0.9 %	0.4 %
Total N	0.1 %	0.11%
Total extractable C	10.0 %	62.0 %
Total Carbon	7.3 %	42.4 %

distillation. Solvent extractables were quantified gravimetrically after being refluxed five times with the respective solvents in a Soxhlet apparatus. Residues were heated at 750 C to determine ash content. Total sulfur was ascertained by an iodometric titration of SO_2 after oxidative combustion using a Leco induction furnace. Total N was found by Nesslerization following ammonification of all N sources with a $H_2SO_4:K_2SO_4$ mercuric oxide solution (modified from Bremner, 1965). Wet combustion with potassium dichromate and $H_2SO_4:H_3PO_4$ was used to determine C by gravimetric analysis of CO_2 evolution (Allison _et al._, 1965). Metals were measured using atomic absorption spectrophotometry following a HNO_3-H_2O_2 digestion of each sludge.

Greenhouse Procedures

Plastic greenhouse pots (15 cm diameter and 15 cm deep) were filled with 2,000 cm^3 of premixed sludge-amended soils. A randomized complete block design was used with loading rates of 0, 5, 10 and 20% by volume for each of 4 soils and 3 replications of each treatment. Loading rates were comparable to 0, 9 x 10^4, 1.8 x 10^5 and 3.6 x 10^5 kg/ha, respectively. The pots were uniformly fertilized with 1 g of 17-17-17 per pot incorporated into the top 2.5 cm. The soils were moistened with rainwater, and 100 ryegrass seeds (_Lolium multiflorum_ Lem.) were planted in each pot. Ryegrass was chosen to represent a rapidly growing cool season pasture grass. Care was taken to minimize the material lost by leaching. Seedling counts were begun four to six days after planting. These continued three times per week until emergence ceased. Emergence counts were done for the first two plantings in the refinery sludge amended soils and for the first 5 plantings in the petrochemical sludge amended soils. Emergence counts were discontinued when the emergence rates approached the control. Thirty to forty days after planting, the plants were harvested by cutting at the soil surface. Harvested plant material was dried at 60 C and weighed. Soils were mixed to simulate cultivation and allowed to dry for two to four weeks. The soil-sludge mixtures were then rewatered and replanted with 100 ryegrass seeds per pot. A second fertilizer application of 1 g of 17-17-17 per pot was made just after the seventh harvest. A total of eight harvests were made.

Soil wettability was measured on two occasions by recording the time necessaary for the air dry soil or soil-sludge mixture to adsorb one drop of distilled water. Triplicate measurements were made on each pot.

All statistical analyses were done using analysis of variance followed by a Duncan's Multiple Range test at the 5 percent level of significance.

RESULTS AND DISCUSSION

Effect of Loading Rates on Emergence

As shown in Figure 1, the high loading rates of refinery sludge appeared to slightly though not

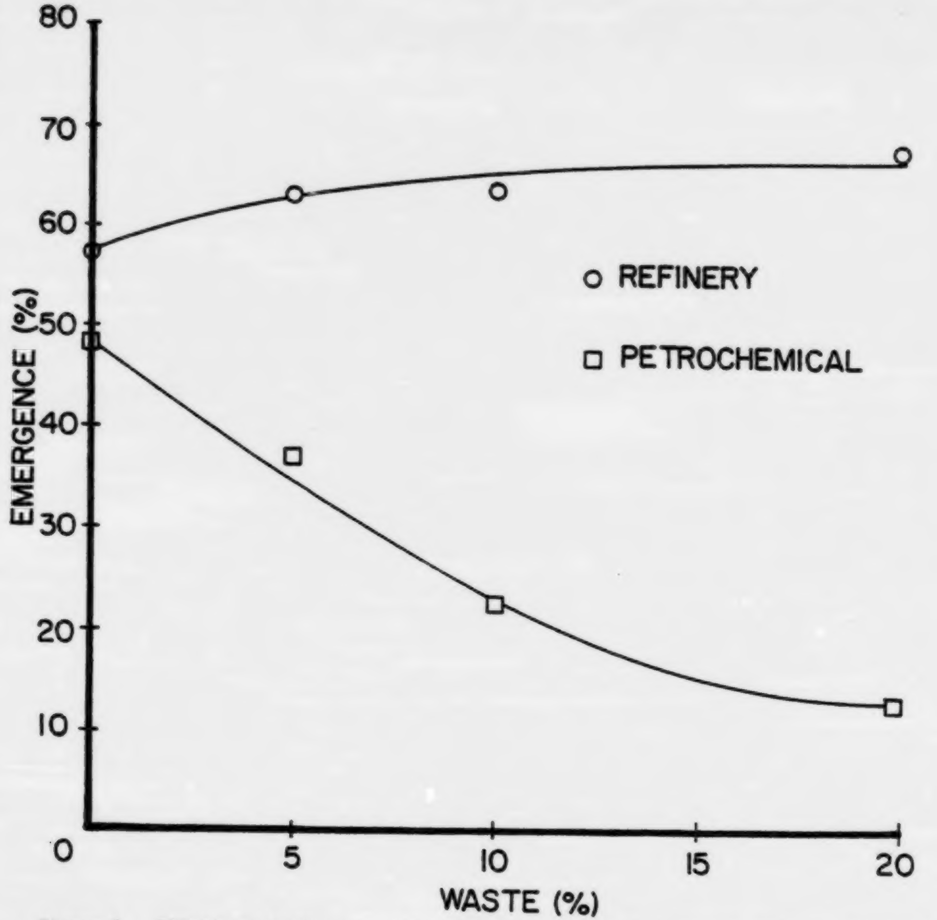

Figure 1. Effects of Refinery and Petrochemical Waste Application Rates on Ryegrass Emergence.

significantly enhance ryegrass emergence. The petrochemical sludge had quite the opposite effect and severely inhibited emergence. Emergence in the 20% loading rate treatment was only 25% of that of the control. The five and 10% loading rate treatments also depressed emergence rates significantly below the control. One potential cause for the lower emergence rates was increased water repellency of the petrochemical sludge-amended soils due to the high saturated hydrocarbon content of this waste. The net result of mixing the sludge with soil was to make the soil more hydrophobic and, therefore, reduce plant available water.

Another possible reason for the low emergence rates in the petrochemical sludge-amended soils is the potential phytotoxic effect of some sludge constituents. Low molecular weight aromatics in particular have been shown to be toxic (Baker, 1970). The aromatic loading rates, estimated as the pentane extractable fraction, are shown in Table 3.

TABLE 3. PERCENT BY WEIGHT OF AROMATICS APPLIED TO SOILS

Waste	REFINERY			PETROCHEMICAL		
Loading Rate (% v/v)	Loading Rate (%v/v)	Total C (%w/w)	Pentane Extractable (%)	Loading Rate (%w/w)	Total C (% w/w)	Pentane Extractable (%)
0	0	0	0	0	0	0
5	6.1	0.61	0.44	5.8	3.60	2.26
10	12.2	1.21	0.87	11.5	7.13	4.53
20	24.4	2.42	1.75	23.0	14.26	9.06

The aromatic content of the 5% v/v petrochemical sludge mix was only slightly greater than that of the 20% v/v refinery sludge loading rate; however, average emergence from the 5% petrochemical sludge amended soils was significantly less than that from the 20% refinery sludge mix (Figure 1). Therefore, the higher aromatic content of the petrochemical sludge is apparently not the only factor involved. Another possible cause of reduced emergence in petrochemical sludge-amended soils may be the presence of herbicidal constituents in the sludge. Except for Ni in the highest application rate of the petrochemical sludge, heavy metal toxicity is not suspected due to the small amounts of sludge added.

Effect of Sludge Aging on Emergence

Emergence of successive plantings in petrochemical sludge-amended soils increased for each successive planting, so that by six months after application, the emergence from all treatments was nearly equal to that of the control. Qualitative observations during the first six months included the continued hydrophobic character of the sludge-amended soils. The loss of odor after two months suggested a decrease in volatilization of compounds which likely contributed to the suppressed emergence. The leachate was clear, and although it was not analyzed, it appeared to be free of organics. The decline in emergence at day 116 was attributed to high greenhouse temperatures during July which may have had a greater impact on the treated soils. Except for this date, emergence rates increased steadily so that by 200 days after application, all treatments were approaching 80-100% of the control.

Effects of Loading Rates on Yield

Table 4 shows that the average yields from the first harvest decreased at all loading rates of either sludge. Since the yield at a given loading rate depended on the sludge applied, one or more of the sludge constituents must have suppressed plant growth. A comparison of the 20% refinery sludge application to the 5% petrochemical sludge application demonstrated the possible influence of total carbon and aromatic content of the sludge on yield (Table 5). Several investigators (Carr, 1919; Plice, 1948; Schwendinger, 1968; Udo and Fayemi, 1975) have concluded that yield reductions are partially due to impaired aeration and to poor water and nutrient availability. Additionally, as cited by Baker (1970), twelve carbon aromatics are highly phytotoxic. The statistical analysis of the yields from these two treatments (Table 5) revealed no significant difference between the 0.9 g/pot from the 20% refinery sludge amended soil and the 1.2 g/pot from the 5% petrochemical sludge amended soils. Thus, there is a strong indication that either the total carbon or aromatic content or both may be limiting the yield.

Nickel content of the 20% petrochemical sludge treatment may be responsible for some of the yield reduction.

TABLE 4. RELATIVE YIELDS OF SLUDGE AMENDED SOILS FROM THE FIRST HARVEST (34 DAYS FOLLOWING APPLICATION) AND THE 8TH HARVEST (437 DAYS FOLLOWING APPLICATION)

Percent Waste	Bastrop Day 34	Bastrop Day 437	Lakeland Day 34	Lakeland Day 437	Nacogdoches Day 34	Nacogdoches Day 437	Norwood Day 37	Norwood Day 437
				REFINERY				
0	100a *	100a	100a	100a	100a	100a	100a	100a
5	49b	91ab	78ab	80ab	64ab	107a	65b	81a
10	30c	77b	35b	87a	37bc	78b	45c	93a
20	22 c	74b	23b	85a	13c	67b	22d	103a
				PETROCHEMICAL				
0	100a	100a	100a	100a	100a	100a	100a	100a
5	27b	87ab	55ab	101a	29b	104a	2b	56ab
10	3c	55b	1b	97a	1c	77b	0b	44b
20	0c	54b	0b	60b	0c	46c	0b	24b

* Values in a given column followed by the same letter do not differ significantly at the 5% level.

TABLE 5. COMPARISON OF YIELDS TO WASTE FRACTION LOADING RATES

Waste	Loading Rate (% v/v)	Total C (% w/w)	Pentane Extractable Aromatics (% w/w)	Average Yield (g/pot)
Refinery	20	2.42	1.75	0.9a
Petrochemical	5	3.57	2.26	1.2a

* Values followed by the same letter do not differ significantly at the 5% level.

Mitchell et al., 1978 report that 80 and 320 ppm Ni in calcareous soils decreased wheat yields by 15 and 25%, respectively. Calculation of the Ni added shows the soil content to be 183 ppm. Thus, one might expect a 20% yield reduction assuming ryegrass has a similar response to nickel levels in the soils. Table 4 shows over 50% yield reduction for the 20% petrochemical sludge application which is clearly greater than expected from the elevated Ni levels. In addition, Ni toxicity would not be expected to decrease over time as observed in subsequent plantings.

Effect of Sludge Aging on Yields

Degradation of the organic fraction of the sludge apparently controlled yields as shown in Table 4. Yields as a function of time are similar to decay curves for mixed composition organics (unpublished data). After an initial lag time evidenced by low yields, there was a period of rapid movement (Figure 2). Apparently, however, very slowly degradable oil materials restricted the yields to levels significantly below those of the control. It appears that this stabilization plateau is a critical factor in the management of land treatment systems. Further research is needed to determine the composition of the resistant hydrocarbon compounds and their rate of decomposition in order to estimate their build-up in soils as a result of repeated sludge applications.

Obviously the soil type will be a factor influencing degradation rate. As shown in Table 4, the Norwood and Lakeland series had inactivated the refinery sludge within

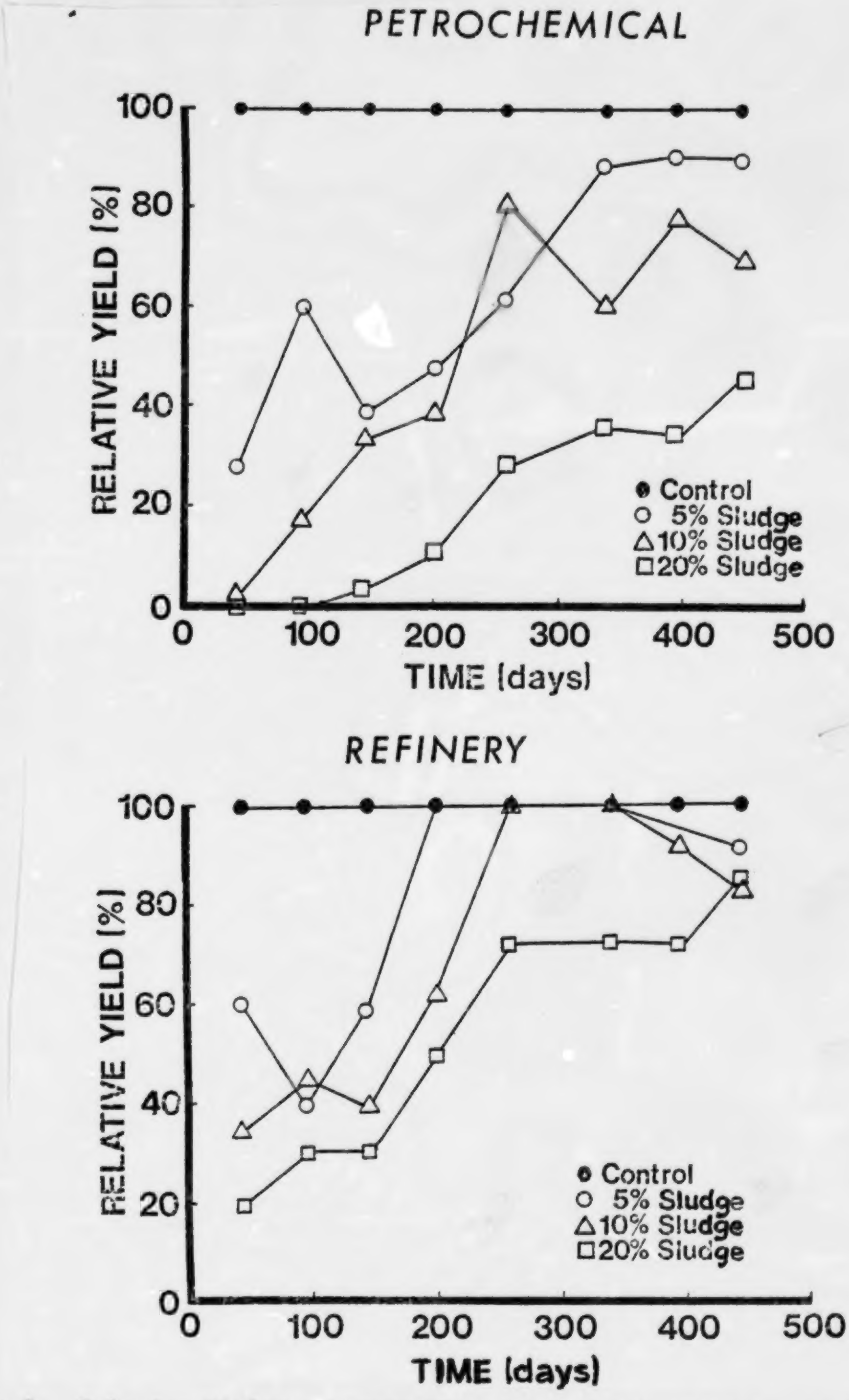

Figure 2. Relative Yields of Ryegrass with Time from Refinery and Petrochemical Sludge Amended Soils.

13 months, and yields on these two soils were back to normal. Likewise, these same two soils appeared to be inactivating the petrochemical sludge faster than the other soils. Since the Bastrop and Nacogdoches soils have higher clay contents, aeration may be a controlling factor in the rate of sludge inactivation.

Soil Wettability

During the course of the experiment, it was observed that soils treated with higher rates of sludge tended to form balls or clods often coated with a dark residue and water applied to these soils ran rapidly between the clods and drained without adequately wetting the sludge-amended soil. To evaluate and quantify the water repellency, wettability tests were performed 10 and 12 months after treatment (Table 6). Comparison of the two tests show no significant decrease in absorption time and indicate that the organics causing the water repellency in the soil at that time were not being rapidly degraded. Since yields from higher application rates were levelled off at this time also, the yield reductions are likely caused by impaired water relations due to the slowly degradable hydrophobic hydrocarbons.

SUMMARY

Concentrations of refinery sludge at 5% v/v (9 x 19^4 kg/ha) and above depressed ryegrass emergence and yield through two mechanisms. Phytotoxic constituents initially acted to retard plant growth. Several months were required for the sludge to degrade sufficiently to allow normal plant growth. Subsequent yield reductions resulted from impaired water relations associated with residual hydrophobic hydrocarbons.

The petrochemical sludge had higher concentrations of both organic carbon and aromatics which suppressed emergence and yield proportional to the amount of sludge applied. The suppression lasted longer than that caused by the refinery sludge applied. Seedling emergence from soils treated with 20% refinery sludge did not differ from that in the unamended control by the second planting, but the corresponding treatments with the petrochemical sludge resulted in depressed emergence for the first five plantings. Grass yield from the 20% refinery sludge treatment required 13 months to reach control levels. The corresponding petrochemical treatment yield reached only 47% of the control 17 months after application.

TABLE 6. AVERAGE ABSORPTION TIME OF WATER DROPLETS APPLIED TO SLUDGE-AMENDED SOILS MEASURED 291 AND 350 DAYS FOLLOWING SLUDGE APPLICATION (VALUES REPORTED ARE AVERAGES OVER ALL SOILS)

	ABSORPTION TIME (SEC)			
Loading Rate (%)	Refinery Waste		Petrochemical Waste	
	Day 291	Day 350	Day 291	Day 350
0	0.6c*	0.6c	1.3b	0.7d
5	8.2bc	16.4bc	27.1b	36.8c
10	35.4b	37.6b	124.1a	80.6b
20	75.8a	66.8a	149.8a	107.2a

* Values in a given column followed by the same letter do not differ significantly at the 5% level.

Though oily sludge may initially be phytotoxic and reduce the yield of emerging vegetation, the toxicity diminishes with time, so that soils used for land treatment of oily sludges can eventually be revegetated.

SECTION 5

BIODEGRADATION STUDY

INTRODUCTION

By optimizing application rates and the controllable environmental parameters, biodegradation of hydrocarbons by soil microorganisms may be maximized, thus making land treatment an environmentally acceptable alternative for disposal of certain organic sludges. Previous studies by Francke and Clark (1974) reported degradation rates up to 100 bbl/ac/mo when used crankcase oil was applied to fertilized soils; however, a study by Raymond et al. (1976) found rates of oil biodegradation to be no greater than 20 bbl/ac/mo. The rate and extent of the biodegradability of an oily sludge is dependent upon the relative proportions of susceptible and recalcitrant hydrocarbons (Bartha and Atlas, 1973). The biodegradation rate of an oily waste in soils was doubled with the addition of nitrogen and phosphorus (Kincannon, 1972) while a separate study by Raymond et al. (1976) showed that the addition of fertilizer only increased oil losses following prolonged incubation as compared to unfertilized soils. In addition, Dibble and Bartha (1979a) found that higher sludge application rates favor the biodegradation of the more recalcitrant aromatic and asphaltic fractions.

The discrepancies between the degradation rates evaluated in earlier studies is considered to be a function of the varying composition of the waste and the properties of the receiving soil. In an attempt to rectify these variances, we have utilized both a refinery and petrochemical sludge to evaluate the effect of several environmental parameters on sludge degradation in four different soils. The parameters evaluated included soil texture, soil moisture, incubation, temperature, application rate, application frequency, and nutrient additions.

The rate of degradation was evaluated by monitoring the rate of CO_2 evolution and by determining the concentrations of residual hydrocarbons in the soil after incubation. This procedure for evaluating sludge degradation was designed as a simple, inexpensive method of determining the optimum environmental conditions in the laboratory prior to field application. Some investigators have chosen to verify substrate degradation as CO_2 evolution by ^{14}C labeled substrates. In this study, we elected instead to verify degradation by hydrocarbon extraction due to the complex nature of the sludges and the relative insignificance of verifying the degradation of one of a large number of substrates. Labeled substrates are more useful for monitoring the degradation of a specific compound. Evaluating the degradation rate of only one substrate of a complex mixture can result in misleading data if the substrate degrades at a rate which differs significantly from the mixture as a whole. Evaluating the degradation rate of a complex mixture by monitoring CO_2 evolution and residual hydrocabrons can produce information defining the average degradation rate of the entire mixture or the degradation rate of a subfraction of the mixture.

MATERIALS AND METHODS

Soil

The same four soils used in the phytotoxicity studies were used in the biodegradation studies. Their physical properties are reported in Table 1 and their chemical properties in Table 7. Nitrogen content was estimated from the organic fraction, while the other nutrients were determined on an ammonium acetate extract. The Norwood sandy clay was used for detailed studies in which all the

TABLE 7. CHEMICAL CHARACTERISTICS OF SOILS UTILIZED IN BIODEGRADATION EXPERIMENTS

Soil Series	N	P	K	Ca	Mg
			ppm		
Bastrop	160	25	200	2,920	385
Lakeland	42	20	200	600	100
Nacogdoches	47	3	164	1,280	400
Norwood	70	94	312	>4,000	485

parameters were evaluated at several levels. The other three soils were studied only at the optimum level of each controlled parameter.

Waste

The same sludges used in the phytotoxicity studies were used for the biodegradation studies. A detailed analysis of the sludges are presented in Table 2. Total carbon of the two wastes was determined by wet combustion to be 7 and 42% for the refinery and petrochemical wastes, respectively. The nitrogen content of each waste was determined by the Kjeldahl method described by Bremner, 1965. The refinery waste contained 0.1% N while the petrochemical waste had 0.11%. The refinery waste and the petrochemical waste contained 21.4% and 12.5% decantable liquid, respectively. To facilitate handling and assure that representative amounts of these fractions of the waste were applied to each treatment, the liquid phase was decanted from each waste, and each component was measured separately and recombined prior to application.

Water content was determined by distillation, and the solvent extractables were quantified gravimetrically following Soxhlet extraction with the respective solvents. Pentane, benzene and dichloromethane were used to extract the saturates, aromatics and asphaltics, respectively. Residues were heated at 750 C for ash content. Wet combustion with potassium dichromate and H_2SO_4:H_3PO_4 yielded total C by gravimetric analysis of CO_2 evolution.

Selected soil samples were analyzed for residual hydrocarbon content following incubation in the soil respirometer. A 25 g sample was mixed in a Waring blender with 25 g anhydrous Na_2SO_4. To this, 150 ml of 15% diethyl ether in dichloromethane was added and blended for one minute. The solvent was decanted and filtered using a Buchner funnel and Whatman No. 42 filter paper. This extraction was repeated twice with 50 ml of the ehter:dichloromethane mix and transferred to another Buchner funnel. The extract was refiltered unitl all soil particles were removed and then transferred with rinsing into a tared round-bottom flask. The solvent was evaporated in a Brinkman-Buchi Rota-Vapor-R* and the extractable hydrocarbons determined gravimetrically. Hydrocarbon extracts were separated into subfractions following the procedure of Warner et al. (1976).

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*Mention of brand name does not constitute endorsement.

Biodegradation

The degradation rate of various waste constituents was determined in a laboratory study in which waste-soil mixtures were placed in a respirometer and incubated at a controlled temperature. A schematic diagram of the respirometer is given in Figure 3. The respirometer is an apparatus which allows temperature and moisture to be kept at a constant level while other parameters, such as treatment rate and frequency, are varied. A stream of humified CO_2-free air is passed through the flasks and the evolved CO_2 collected in columns containing 0.1N NaOH. The air stream is purified within a scrubber system consisting of a reciprocator pump (Reciprocator Co., Copenhagen, Denmark), and a series of flasks, one with concentrated H_2SO_4, two parallel flasks of 4N NaOH, and a pair of flasks in series containing CO_2-free water. The two flasks of 4N NaOH are placed in a parallel position so that the air stream may be switched to a fresh solution without interrupting the flow of air. Between the scrubber and each

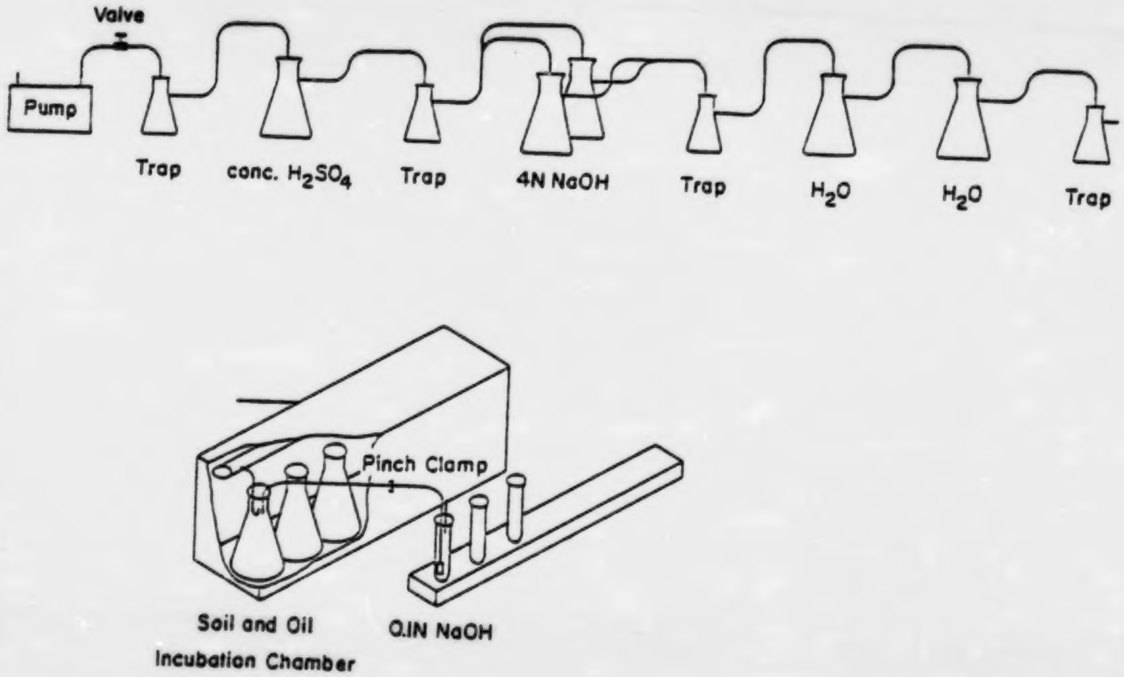


Figure 3. Schematic diagram of a respirometer.

flask is a manifold which distributes the air to the flasks through equal length capillary tubes, thus providing an equal flow rate for each flask. Each incubation chamber should include two empty flasks which serve to monitor impurities in the air stream. The air leaving each flask is passed through a 12 mm coarse Pyrex gas dispersion tube which is positioned near the bottom of a 25 x 250 mm culture tube containing 50 ml of CO_2-free 0.1N NaOH. The rate of CO_2 evolution is used as an indication of microbial activity and relative waste decomposition (Stotzky, 1965). Upon termination of the experiment, the soil-waste mixture was removed from the flask, and subsamples were taken for the determination of residual hydrocarbon content and for an estimation of the microbial population. When this data is combined and evaluated, information is obtained which can provide guidance in gauging application rate and frequency, the rate of nutrient addition, and the rate of waste degradation in different soil types or temperatures. The determination of these parameters before field application can prevent an overloading of the system or an unnecessary addition of mineral nutrients.

Each hazardous waste stream possesses a variety of toxic and recalcitrant compounds, and a unique ratio and concentration of mineral nutrients. Therefore, the study began with the collection of representative samples of the waste and soil. Soil collected from the field for the respiration study was maintained at field capacity (about -1/3 bar moisture tension) and stored at room temperature under a fixed relative humidity in order to preserve the soil microcosm. Soil collected where water content was above field capacity was air dried to reach field capacity, while soil which was collected below field capacity was wetted with distilled water to field capacity. The collection of a truly representative waste sample is also critical to the production of valid data in the laboratory study, although few if any waste streams will exist as homogeneous mixtures or will be of uniform composition with time. Each waste was stored at 4 C until use. At this time, the liquid and solid phases were separated and recombined at a predetermined rate.

The respiration experiment was begun by equilibrating the respiration chamber to the desired temperature and starting the scrubber system at least 24 hours prior to the addition of soil. Two days prior to waste addition, the soil was allowed to air dry or was wetted with distilled water to the desired moisture content. A 100 g dry weight soil sample was then placed on a glass plate and crushed to a uniform particle size consistency of approximately 1/4 inch. The soil was not air dried or passed through a sieve, as this would have altered the nature of the microbial population of the soil. The crushed and weighed soil sample was then placed into a 500 ml Erlenmeyer flask, which was then connected to the CO_2-free air stream and to a column which contained 0.1N NaOH. The flow of air through the chamber was adjusted so that neither stimulation of microbial activity nor inhibition occurred. After the soil had been placed in the respirometer and allowed to equilibrate for at least 48 hours, a 20-40 g subsample of soil was removed from the flask and placed in an evaporating dish. Waste was then mixed with the soil on a percent weight basis. After mixing, the waste-soil subsample was mixed with the total soil sample from the flask and replaced in the preweighed flask which, in turn, was again placed in the respirometer. This mixing procedure was also used to add water, or to reapply the waste during the respiration experiment.

Soil Moisture

The rate of degradation of both the refinery and the petrochemical waste (at an application rate of 1%) was evaluated in four soils maintained at field capacity (-1/3 bar). Field capacity for the four soils was 18%, 5%, 22%, and 20% for the Norwood, Lakeland, Bastrop, and Nacogdoches soils, respectively. In addition, samples of the Norwood soil were tested at moisture contents of 33% (0 bar) and 12% (-15 bar). The incubation flasks were weighed periodically and moisture content adjusted as needed.

Temperature Effects

The effect of temperature on degradation of the two sludges was studied by incubation of the Norwood soil-sludge mixtures at 10, 30 and 40 C. Each waste was studied at a 1% loading rate at each temperature.

Application Rates

Application of oil sludge to soils was studied at treatment rates of 0.1, 0.5, 1, 5, and 10 g of sludge per 100 g dry weight of soil, equivalent to a hydrocarbon loading of 10, 50, 100, 500, and 1000 mg refinery or 62, 124, 610, 3100, and 6200 mg petrochemical waste. These treatment rates of 0.1, 0.5, 1, 5, and 10 g soil approximate field loading rates of 2.2×10^3, 1.1×10^4, 2.2×10^4, 1.1×10^5, and 2.2×10^5 kg sludge/ha, respectively, assuming uniform incorporation to a depth of 15 cm. Control soils to which no sludge had been applied were included in each study to monitor the respiration rate of the indigenous soil microoorganisms.

Application Frequency

Two experiments were conducted to determine the effect of repeated applications of waste sludge on the degradation rates. In the first experiment, reapplications of the petrochemical waste were made following 180 days of decomposition, corresponding to the initial application rates of 0.1, 0.5, 1, and 5 g per 100 g soil. In the second experiment, reapplications were made at a rate of 5 g per 100 g soil 45, 90, and 135 days after the initial application to two flasks of each waste and 90 days after the initial application to one flask of each waste. One flask of each waste served as a control receiving 5 g per 100 g soil at the beginning of the experiment.

Mineral Nutrients

The C:N ratio of the refinery and petrochemical wastes was determined to be 78:1 and 381:1, respectively. In an attempt to increase the microbial activity and enhance waste degradation, mineral nutrients were added in the form of $CaNO_3$, KCl, and $CaPO_4$. These were mixed with the soil prior to addition of the wastes to achieve the desired treatment ratios. The refinery waste was tested at C:N ratios of 78:1, 40:1, and 9:1 and at a C:K and C:P ratio of 40:1. In addition, one flask was supplied with N, P, and K at a rate of 40:1. Degradation of the petrochemical waste was evaluated at C:N ratios of 380:1, 124:1, and 23:1. The C:P and C:K ratios of the soils in two flasks were adjusted to 124:1, and the soil in another flask was adjusted to 124:1 for all three nutrients.

Microbial Analysis

Following incubation for 180 days, selected soil samples were removed for microbial analysis. Soil samples were assayed on six different media to determine the effect of waste application on the soil microcosm. Soil bacteria were enumerated using plate count agar (Difco) and soil extract agar (Odu and Adeoye, 1969) with 10 mg/l of Amphoteracin B. The presence of soil fungi was determined using potato dextrose agar (Difco) and soil extract agar with 30 mg/l rose bengal and streptomycin. Hydrocarbon utilizing bacteria and fungi were detected by replacing the carbon source used in soil extract agar with 6.25 g/l Silica Gel Oil as suggested by Baruah *et al*., 1967. The Silica Gel Oil was made by combining 5.0 g of that waste and 1.25 g of fumed Silica Gel (Car-o-sil, Cabot Corp., Boston, Mass).

One gram of the incubated soil was placed in 99 ml of phosphate buffer and shaken vigorously for one minute. Subsequent dilutions were made by adding 1 ml of the previous dilution to 99 ml of phosphate buffer. In order to retard spreading of mobile organisms, 0.5 ml of each dilution was added to 2.5 ml soft agar, mixed using a vortex mixer, and poured onto the agar surface. Plates were incubated for a minimum of 2 weeks at 40 C; the same temperature at which the soil waste mixture had been incubated. All plates were assayed in quadruplicate.

The total populations of bacteria and fungi were estimated using a pour plate method. Specific groups of microorganisms in the soil were not evaluated because this information was considered to be irrelevant to the degradation of a complex mixture which requires a diverse range of organisms to cometabolize the various waste constituents. Instead, total soil heterotrophic bacteria and fungi, in addition to hydrocarbon utilizing organisms, were estimated to provide an indication of the effect of waste addition on these populations. Autotrophic organisms were not enumerated because it was believed that CO_2 consumed by microbial activity would be accounted for in the residual hydrocabon analysis. In addition, one of the primary candidates for autotrophic CO_2 consumption, *Thiobacillus denitrificans*, loses the autotrophic behavior when cultivated in an organic medium (Parker, 1957).

RESULTS AND DISCUSSION

Initial results indicated that a flow rate of at least 10 cm^3 of air per minute per 100 g of soil was required to prevent depletion of oxygen in the incubation flasks. Reproducibility of the data was increased when each flask was removed at 45 day intervals and the soil moisture content determined by weighing. When the moisture content of the soil fell below 10% or increased to above 35%, the respiration rate deviated significantly from replicate treatments in which the moisture content had not changed, and such data was rejected. Although a thrice weekly sampling schedule was maintained throughout the study, it appears that the sampling schedule could have been reduced to once a week without sacrificing the quality of the data.

Soil Texture

Four soils were studied to determine their utility as a medium for degradation of oily sludge constituents. Each soil was incubated at 30 C and a moisture content of field capacity. The results are presented in Figures 4 and 5 and in Table 8. For both wastes, the greatest rate of CO_2 evolution occurred in Norwood soil, degradation in the Nacogdoches and Lakeland soils was intermediate, and the least amount occurred in the Bastrop soil. The amount of carbon evolved as CO_2 from petrochemical sludge-amended Bastrop clay was only 8 mg greater than from the unamended soil, which is equivalent to a decrease of only 0.3% total carbon. Thirty-seven percent of the refinery and 13% of the petrochemical waste decomposed from the Lakeland soil during the 100 day incubation period, while 44% and 9% of the refinery and petrochemical sludges, respectively, were decomposed in the Nacogdoches soil. The various rates of decomposition did not appear to be influenced by soil pH (Table 1). This may have been due to the random range of pH in the soils which were studied.

TABLE 8. THE EFFECT OF SOIL TEXTURE ON THE BIODEGRADATION OF REFINERY AND PETROCHEMICAL SLUDGE APPLIED AT A RATE OF 5% (WT/WT) TO SOILS AT FIELD CAPACITY AND INCUBATED FOR 180 DAYS AT 30 C

Soil	Total Carbon Applied (mg)	% Carbon Degraded as Determined by	
		CO_2-C Evolved	Residual C
Refinery Waste			
Norwood sandy clay	350	60	63
Nacogdoches clay	350	44	54
Lakeland sandy loam	350	37	45
Bastrop clay	350	37	47
Petrochemical Waste			
Norwood clay	2,100	15	34
Nacogdoches clay	2,100	9	32
Lakeland sandy loam	2,100	13	30
Bastrop clay	2,100	0.3	19

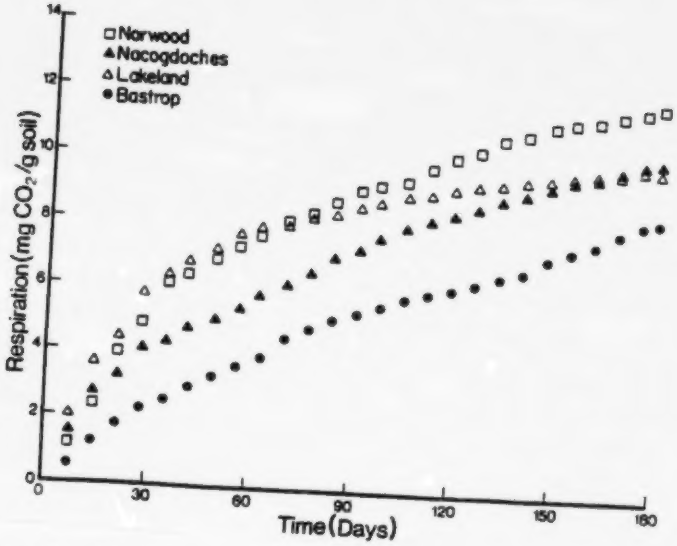


Figure 4. The effect of soil texture on CO_2 evolution from soils amended with 5% (wt./wt.) refinery waste and incubated for 180 days at field capacity and 30 C.

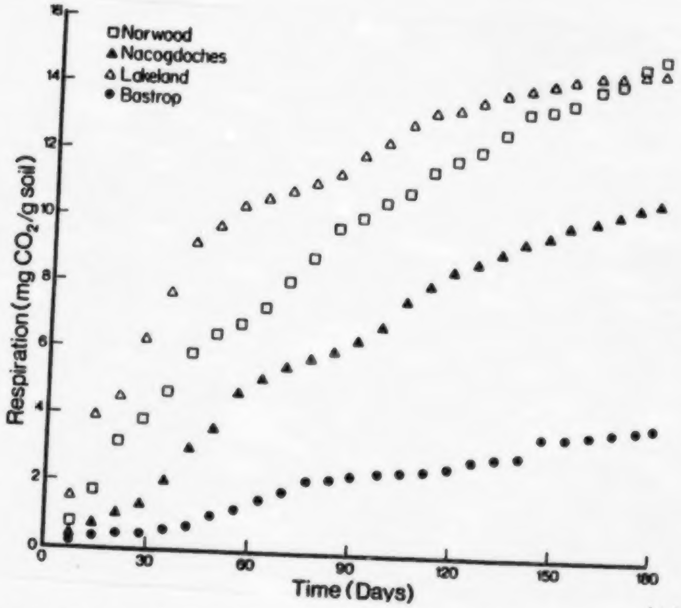


Figure 5. The effect of soil texture on CO_2 evolution from soils amended with 5% (wt./wt.) petrochemical waste and incubated for 180 days at field capacity and 30 C.

The probable reasons for the greater degradation rates in the Norwood soil are the moderate texture of sandy clay (Table 1), good CEC, and nearly ideal moisture relations and aeration. These physical and chemical properties combine to provide an excellent medium for the growth of microorganisms.

Soil Moisture

The influence of soil moisture content on the biodegradation rate of both sludges at 10 C applied to the Norwood soil is shown in Figures 6 and 7. In addition, the influence of soil moisture on the average biodegradation rates at 35 C is given in Figures 8 and 9. The cumulative CO_2 evolution is given in Table 9. For both wastes, the moisture content had a greater relative influence on the rate of biodegradation at 10 C than it did at the higher temperatures. At both temperature regimes, the refinery waste exhibited maximum degradation at 18% soil moisture which represented field capacity. The biodegradation rates were reduced at both wetter and drier moisture contents. For the petrochemical waste, the maximum biodegradation rates occurred at the lowest moisture content at 10 C and

TABLE 9. EFFECT OF MOISTURE CONTENT ON BIODEGRADATION OF NORWOOD SOIL TO WHICH 1% OF THE REFINERY OR PETROCHEMICAL WASTE HAD BEEN APPLIED

Waste	Total Carbon Applied (mg)	Temperature (°C)	% Biodegradation as Determined by CO_2 Evolution Soil Moisture 12%	18%	33%
Refinery	70	10	10	36	21
		30	3	59	47
		40	0	42	14
Petrochemical	420	10	10	9	3
		30	20	18	18
		40	5	13	21

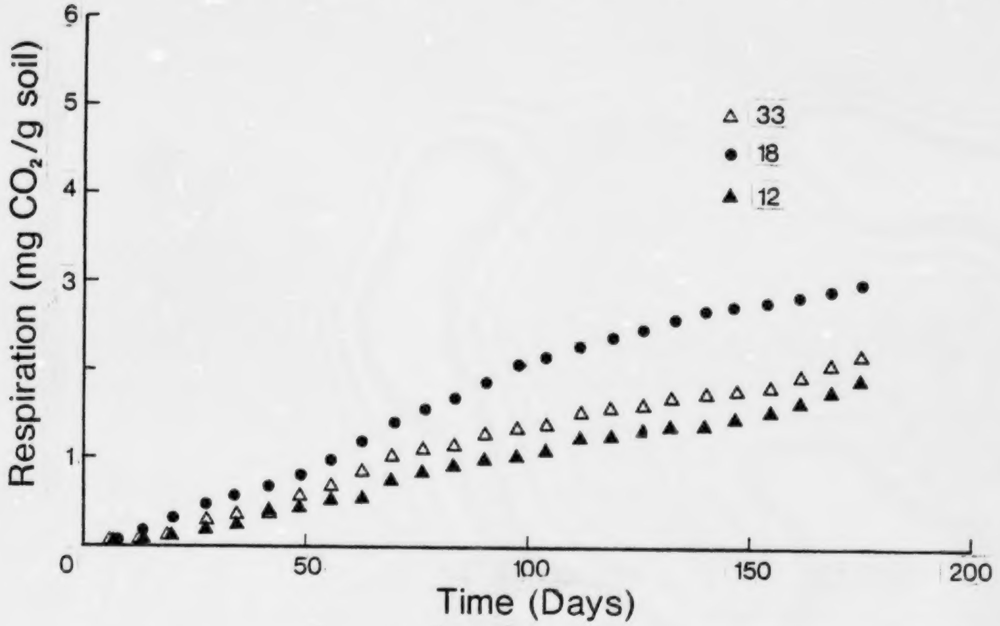


Figure 6. The influence of soil moisture on CO_2 evolution from Norwood soil amended with 1% (wt./wt.) refinery waste and incubated for 180 days at 10 C.

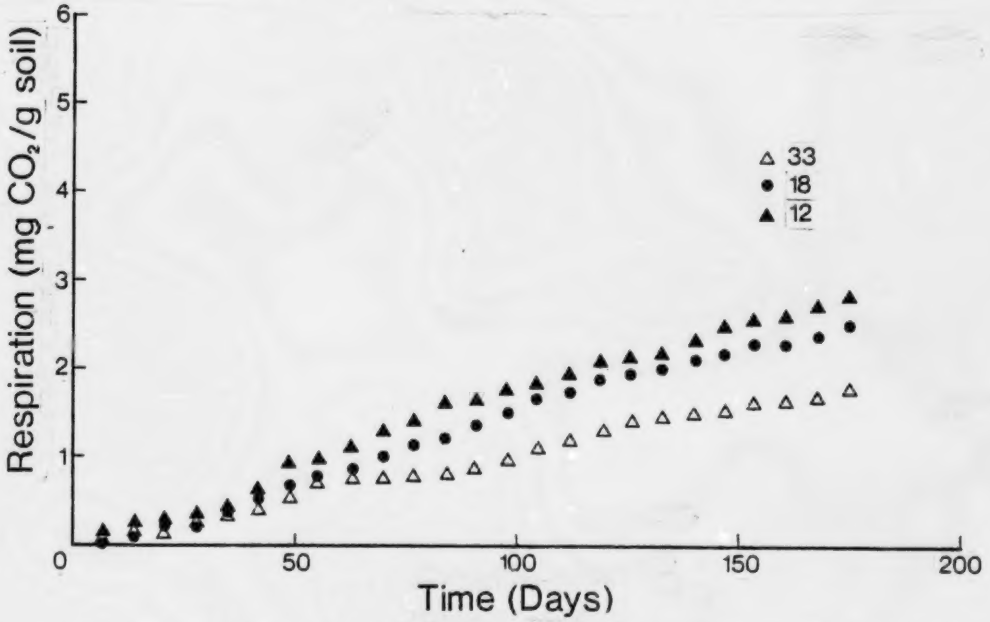


Figure 7. The influence of soil moisture on CO_2 evolution from Norwood soil amended with 1% (wt./wt.) petrochemical waste and incubated for 180 days at 10 C.

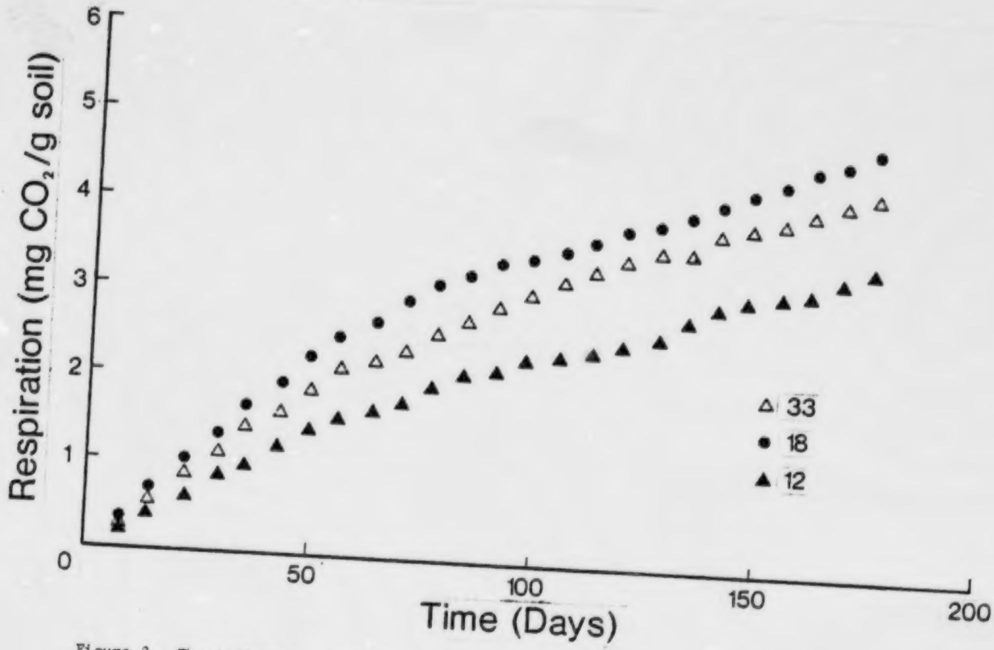


Figure 8. The influence of soil moisture on CO_2 evolution from Norwood soil amended with 1% (wt./wt.) refinery waste and incubated for 180 days at 35 C.

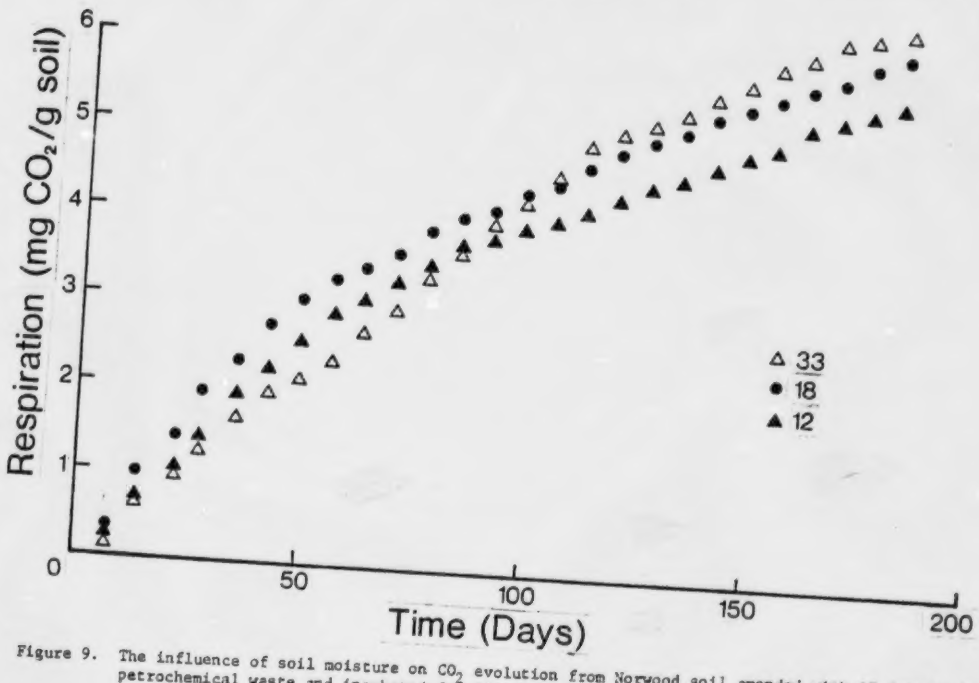


Figure 9. The influence of soil moisture on CO_2 evolution from Norwood soil amended with 1% (wt./wt.) petrochemical waste and incubated for 180 days at 35 C.

the highest moisture content at 40 C. Thus, while field capacity appeared to be within the optimum range of soil moisture for the refinery waste, no such optimum was obvious for the petrochemical waste. For both wastes, there appeared to be a rather broad range of soil moisture contents, including conditions both wetter and drier than field capacity, which had a minimal influence on waste decomposition. Only at excessively wet or dry conditions did the moisture content become a dominant controlling factor on waste degradation.

Temperature

The effect of temperature on CO_2 evolution from waste amended soil is given in Figures 10 and 11, while the rate of degradation is given in Table 10. Both wastes were applied to the soil at a rate of 1%. The evolution of carbon dioxide from Norwood soil treated with both wastes increased with temperature through 40 C. Increases in the respiration rate of the unamended soils between 30 and 40 C were greater than the increase in the rate of the soil to which waste had been added. Therefore, a comparison of the percentages of waste degraded at the various temperatures reveals a reduction percentage of carbon degraded from the waste-soil mixture which was incubated at 40 C. Biodegradation was calculated both from CO_2 evolution and

TABLE 10. THE INFLUENCE OF TEMPERATURE ON CO_2 EVOLUTION FROM SLUDGE-AMENDED SOIL

Waste	Total Carbon Applied (g)	Analytical Method	Biodegradation Percent of Waste Applied 10°C	30°C	40°C
Refinery	0.07	CO_2 evolution	36	59	42
		Residual C	25	62	49
Petrochemical	0.42	CO_2 evolution	9	18	13
		Residual C	12	26	21

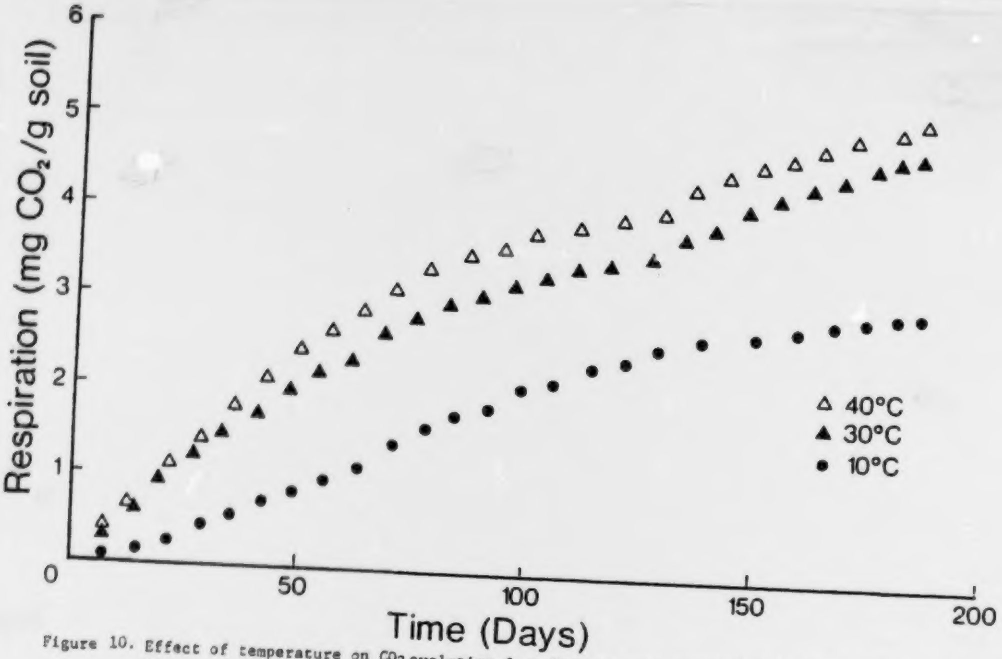


Figure 10. Effect of temperature on CO_2 evolution from Norwood soil amended with 1% (wt./wt.) refinery waste and incubated for 180 days.

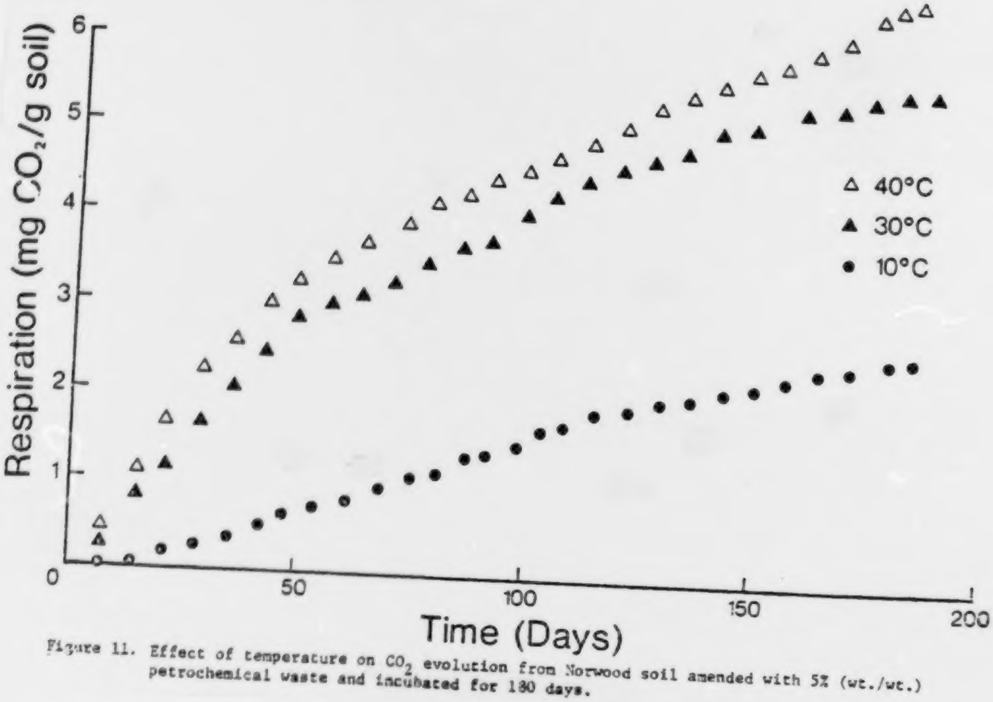


Figure 11. Effect of temperature on CO_2 evolution from Norwood soil amended with 5% (wt./wt.) petrochemical waste and incubated for 180 days.

residual carbon measured by wet combusion. The results given in Table 10 demonstrate reasonable agreement. The wet combustion data will be used here as a basis for discussion. At 30 C, 62% of the refinery sludge and 26% of the petrochemical sludge were degraded, while at 40 C only 49% of the refinery and 21% of the petrochemical sludge were degraded. At 10 C, the residual carbon content was equivalent to degradation rates of only 25 and 12% for the refinery and the petrochemical sludge, respectively.

The biodegradation rate generally doubled between 10 and 30 C but decreased again at 40 C indicating a reduction of microbial activity at the higher temperature. These results are in general agreement with those reported by Dibble and Bartha (1979a) who reported the optimum temperature for degradation of an oily sludge to be above 20 C.

Application Rates

The evolution of CO_2 from soils amended with either waste increased with increasing application rates as shown in Figures 12, 13 and Table 11. Since the data from 30 and

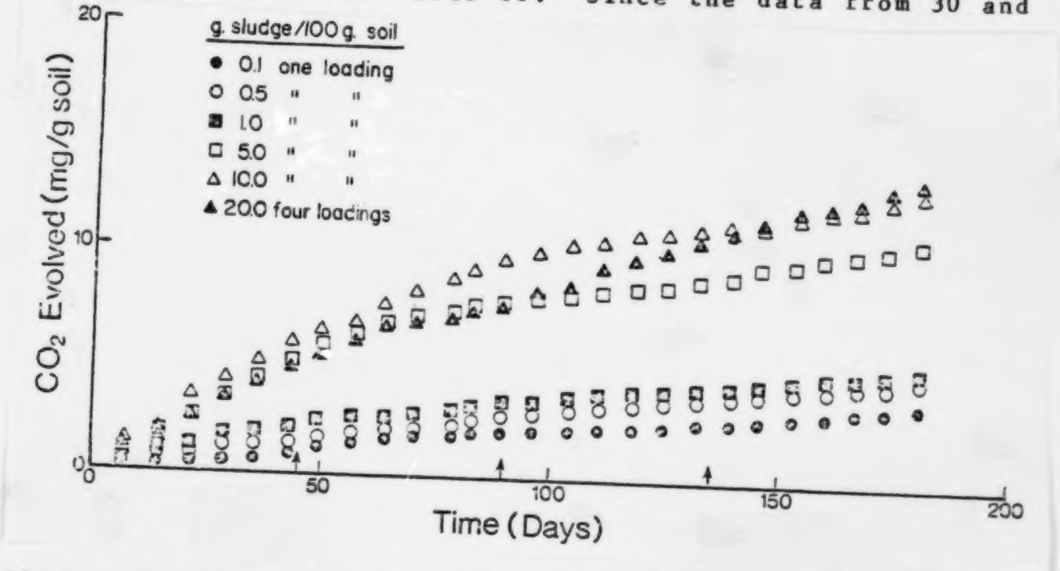


Figure 12. The influence of loading rate on the biodegradation of refinery waste applied to Norwood soil and incubated for 180 days at 30 C and 18% moisture.

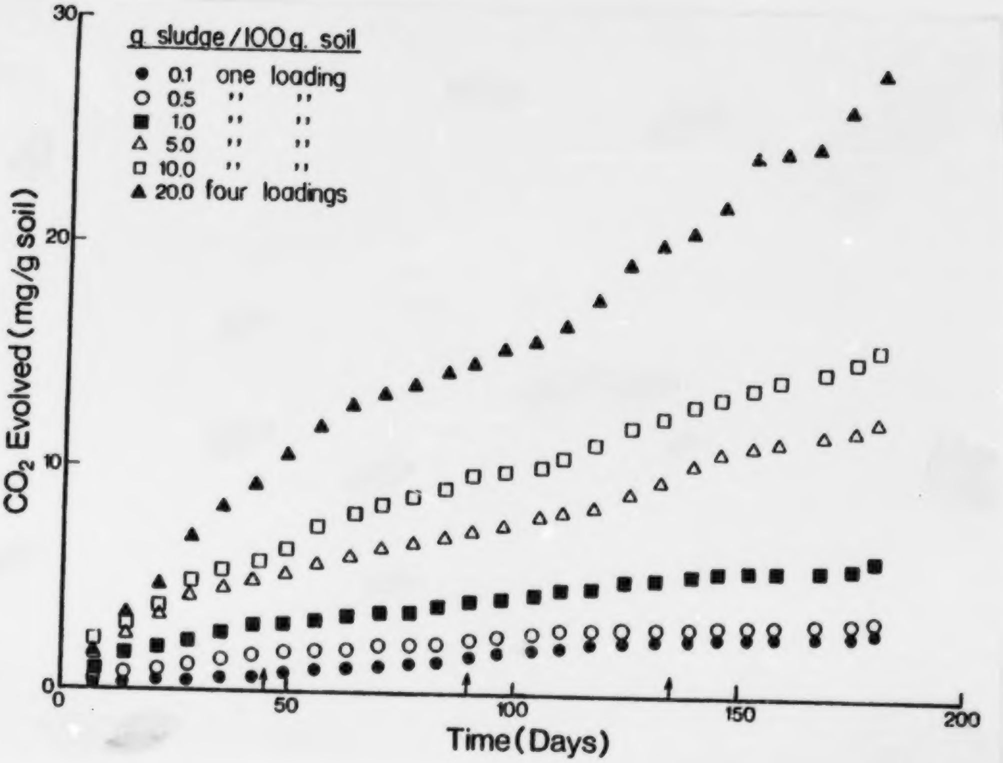


Figure 13. The influence of loading rate on the biodegradation of petrochemical waste applied to Norwood soil and incubated for 180 days at 30 C and 18% moisture.

40 C differed only a little, the average value for these two treatments are shown here. Of the two wastes investigated, a much larger fraction of the carbon applied in the refinery waste was released as CO_2. An average of 47.7% of the carbon applied in the refinery waste was respired, while only 19.8% of the petrochemical waste carbon was released.

When comparisons are made strictly on the basis of the amount of waste applied (Figure 14), it is evident that a greater percentage of the refinery waste was degraded, particularly at the greater application rates. The rate of CO_2 evolution is nearly linear at low rates but appears to be approaching a plateau at the greater rates. This indicates that at higher application rates inhibitory mechanisms may have reduced the percent carbon

TABLE 11. THE INFLUENCE OF LOADING RATE ON THE BIODEGRADATION OF BOTH WASTES APPLIED TO NORWOOD SOIL AND INCUBATED AT 30 AND 40 C AT 18% MOISTURE FOR 180 DAYS

Waste	Loading Rate (%)	Carbon Applied (mg)	% Biodegradation as Determined by Evolved CO_2-C	Average Biodegradation Rate µg CO_2/g/day
Refinery Waste				
1 Loading	0.1	7	15	40
"	0.5	35	85	101
"	1.0	70	51	114
"	5.0	350	60	436
"	10.0	700	41	575
Petrochemical Waste				
1 Loading	0.1	42	10	31
"	0.5	210	9	10
"	1.0	420	16	173
"	5.0	2100	15	524
"	10.0	4200	9	696

degraded, although the absolute rate of decomposition increases.

The greatest fraction of the refinery waste was evolved as CO_2 at the 5% application rate, while the greatest fraction of the petrochemical waste was released as CO_2 at the 1% application rate. The fractions respired do not decrease greatly at a 5% application rate of either waste, but fall at 10%; therefore, applications of between 5 and 10% appear to encompass the maximum degradation rates for the wastes studied.

Application Frequency

Since typical operations in the field will involve repeated applications to the same piece of land, tests were run to investigate the impact of application frequency on CO_2 evolution. A test was run over a period of 180 days using both wastes applied in 5% increments. Applications were made at the beginning of the study to all treatments,

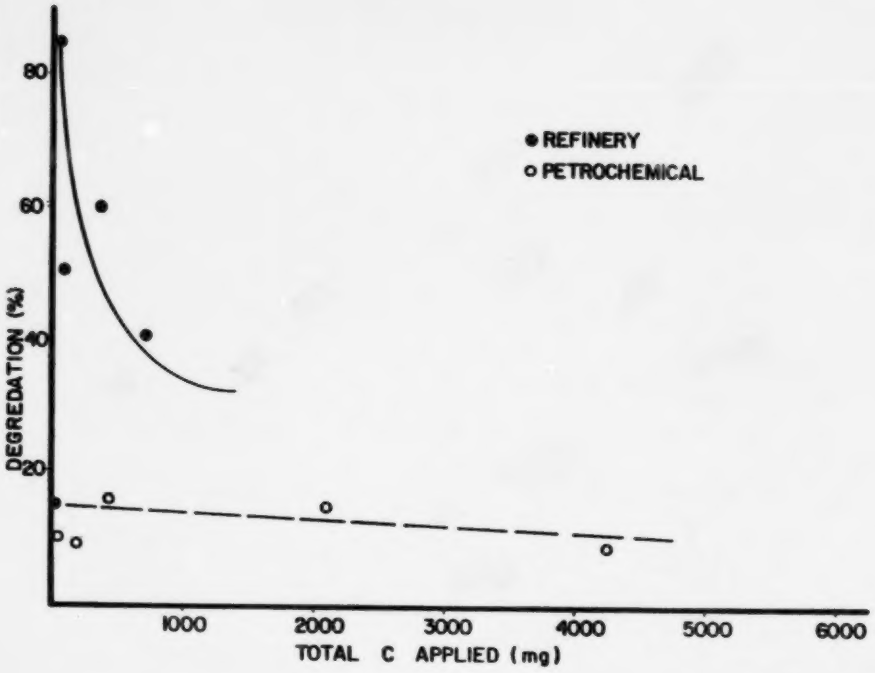


Figure 14. The effect of application rate on the degradation of refinery and petrochemical sludges.

again after 90 days on the treatments that received two applications, and after 45, 90 and 135 days on the treatments that received four applications. The results are presented in Figures 15 and 16 and are summarized in Table 12. Single 10% applications of each waste are also included for comparison. As would be expected, the amount of CO_2 released increased as the amount of waste applied increased. For one 5% application of refinery waste, 63% of the applied carbon was released over the 180 days, while only 27% of the carbon from the four 5% applications was released. Thus, while more carbon was oxidized with more frequent application rates, residual carbon was building in the soil with each subsequent application. The respiration from the single 10% application of the refinery waste and from the two 5% applications were nearly the same. However, when the respiration rates are calculated per unit waste applied per unit time, it is evident that the smaller frequent application resulted in a more rapid rate of biodegradation. The petrochemical waste exhibited the same trend. Thus, it

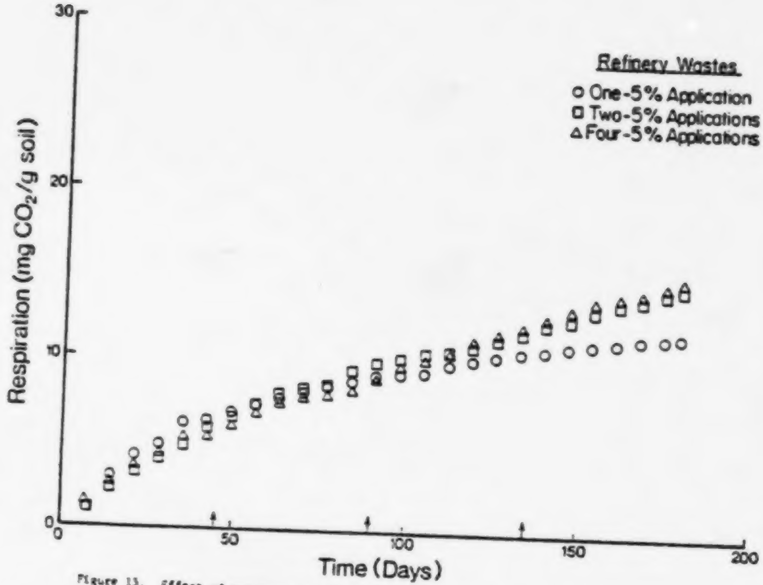


Figure 15. Effect of treatment frequency on the evolution of CO_2 from Norwood soil amended with refinery waste and incubated for 180 days at 30 C and 13% moisture.

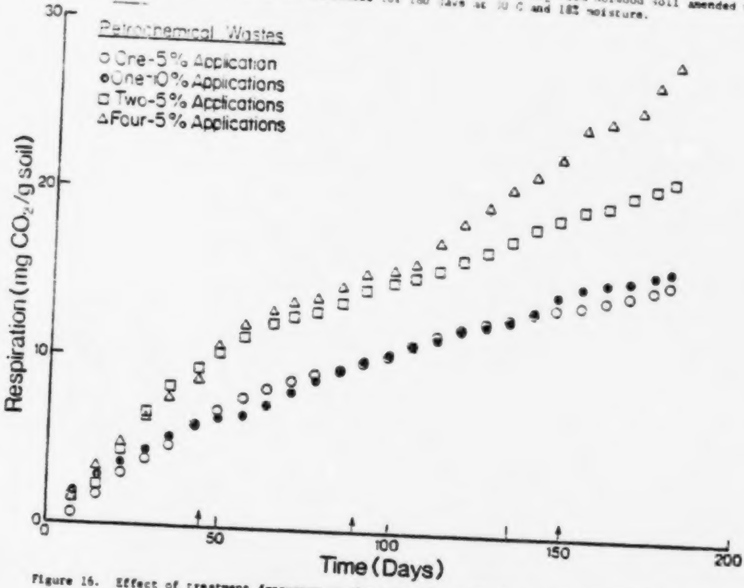


Figure 16. Effect of treatment frequency on the evolution of CO_2 from Norwood soil amended with petrochemical sludge and incubated for 180 days at 30 C and 13% moisture.

TABLE 12. BIODEGRADATION OF TWO WASTES APPLIED TO NORWOOD SOIL AT DIFFERENT FREQUENCIES. ALL SOILS WERE MAINTAINED AT FIELD CAPACITY AND 30 C.

Rate (%)	Numbers of Applications	Total Carbon Applied (mg)	% Biodegradation as Determined by CO$_2$ Evolution	% Biodegradation as Determined by Residual Carbon
Refinery Waste				
5	1	350	63	63
5	2	700	47	46
10	1	700	46	24
5	4	1400	27	34
Petrochemical Waste				
5	1	2100	15	34
5	2	4200	12	32
10	1	4200	9	18
5	4	8400	9	21

appears that frequent, small applications may allow greater rates of biodegradation.

In another experiment, three treatments of petrochemcial waste were incubated for 360 days. These included one treatment in which a 1% waste addition was made at the beginning and after the 180 days, one treatment in which 5% was applied at the beginning and after 180 days, and one treatment in which 10% was applied only at the beginning. The percent carbon evolved as CO$_2$ during the first 180 days, the second 180 days, the total over the 360 day period, and the amount of carbon degraded as determined by wet combustion are given in Table 13. The largest fraction of the applied carbon was degraded at the 1% application rate. The rate of CO$_2$ evolution from the 1% application was essentially the same during the 180 days following the second application as during the 180 days following the first application. Degradation during the 180 day period following the 2nd application when based on the total C applied, was 30 to 50% of the degradation rate

TABLE 13. THE INFLUENCE OF REPEATED APPLICATIONS OF PETROCHEMICAL SLUDGE ON BIODEGRADATION. THE SLUDGE HAD BEEN APPLIED TO NORWOOD SOIL MAINTAINED AT FIELD CAPACITY AND INCUBATED AT 30 C.

Application Rate (%)	Number of Applications	Total Hydrocarbon Applied (mg)	% Degradation of the 1st application during the first 180 days period	% Degradation of the 2nd application during 180 days following second application	% Degradation of the Total C present during the 180 days following second application	% Degradation of the Total C applied during 360 days period	Based on Residual Carbon
1	2	1,240	16	15	7	15	22
5	2	6,200	15	9	4	12	9
10	1	6,200	9	-	3	12	6

during the first 180 day period for the 1 and 5% application rates.

These results also indicate that repeated applications of smaller amounts of waste result in greater amounts of waste being degraded over longer periods of time than can be achieved with a single large application. For the split application of 6,200 mg C/100 g soil, 9% of the applied carbon was degraded; while for the single application, only 6% of that applied was degraded. Even greater percentages of applied hydrocarbon were respired from the split application of 1%, although the total amount of materials degraded was less.

Mineral Nutrients

The influence of nutrient addition on the respiration rates are shown in Figures 17 and 18. The two wastes differed greatly in their C:N ratios. The refinery waste was composed of 78 parts C for each part N, while the petrochemical waste has a C:N ratio of 380:1. For the refinery waste, optimum degradation occurred when the C:N ratio was reduced to 9:1. Addition of potassium at a rate of 40:1, C:K, and supplementation with NPK at a rate of 40:1 did not result in an increase in evolved carbon dioxide when compared to waste amended soil which had no nutrient additions.

The petrochemical waste exhibited a 20% increase in CO_2 evolved as a result of the addition of N alone at a rate of 124:1 or NPK at a rate of 124:1 C:NPK. The addition of greater amounts of nitrogen alone did not result in an

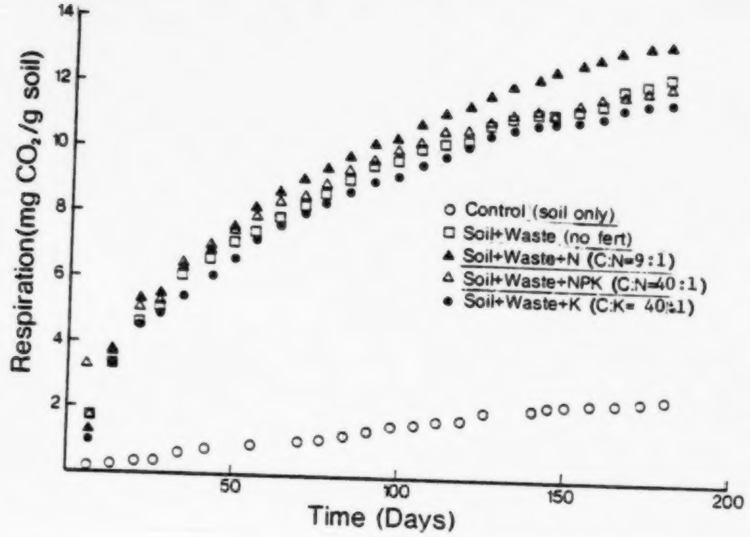


Figure 17. The influence of nutrient additions on the cumulative respiration of Norwood soil amended with 5% (wt./wt.) refinery waste and incubated for 180 days at 30 C and 18% moisture.

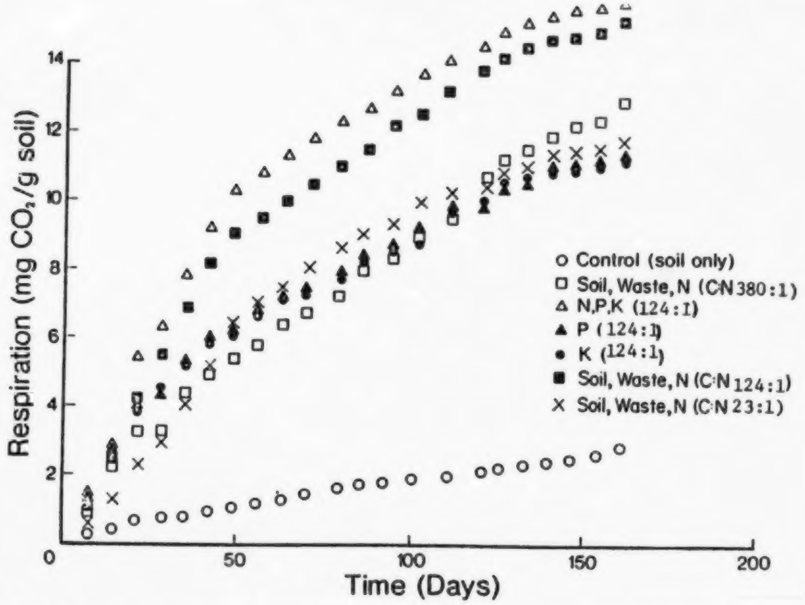


Figure 18. The influence of nutrient additions on the cumlative respiration of Norwood soil amended with 5% (wt./wt.) petrochemical waste and incubated for 180 days at 30 C and 18% moisture.

increase in respiration rates over the unamended waste treatment. As with the refinery waste, the addition of phosphorus and potassium alone did not result in an increase in CO$_2$ evolution. Determinations of residual hydrocarbon for the amended soil 180 days following fertilizer application also indicated increased degradation rates of all treatments greater than that indicated by the cumulative CO$_2$ evolution (Table 14). The addition of nitrogen at a ratio of 9:1, C:N, increased the rate of biodegradation for the refinery waste by alomost 30%. The addition of all three mineral nutrients at a rate of 124:1 C:NPK increased the rate of biodegradation for the petrochemical waste by almost 50%.

Thus the decomposition rate of the refinery waste was increased substantially by adjusting the C:N ratio from 78:1 to 9:1. While the more nitrogen deficient petrochemical waste exhibited an increase in decomposition when the C:N ratio was adjusted from 380:1 to 124:1, this effect was reduced when additional nitrogen was added to raise the C:N

TABLE 14. THE EFFECT OF MINERAL NUTRIENTS ON RESIDUAL CARBON IN WASTE AMENDED SOIL AFTER 161 DAYS INCUBATION

Mineral Nutrients		Residual Hydrocarbon (gm)	% Biodegradation as Determined by	
			Residual Hydrocarbon	CO$_2$ Evolution
Refinery Sludge: Total carbon applied 0.35 g				
None	78:1	0.18	63	60
C:P	40:1	0.12	76	71
C:NPK	40:1	0.14	72	74
C:N	9:1	0.10	80	82
Petrochemical Sludge: Total carbon applied 2.1 g				
None	380:1	2.06	34	15
C:P	124:1	1.76	43	13
C:NPK	124:1	1.56	50	18
C:N	23:1	1.76	43	13

ratio to 23:1. The addition of P and K alone or with nitrogen did not appreciably increase the respiration rates from soils amended with either waste. The lack of increased biodegradation of the petrochemical waste at C:N ratios narrower than 124:1 indicates that factors other than nitrogen were limiting breakdown of the waste.

Other researchers have also reported that the addition of mineral nutrients to waste amended soil offset nutritional imbalances, thus providing a more suitable environment for the microbial utilization of petroleum compounds. Increases in the rate of waste biodegradation have been reported by Cook and Westlak, 1974; Dobson *et al*., 1971; Maunder and Ward, 1975; and Dibble and Bartha, 1979b. When several different oily wastes were applied to soils, Kincannon (1972) found that the rate of biodegradation was doubled when nitrogen and phosphorus were added to the soil with the waste. In a field study on waste degradation in soil, Raymond *et al*. (1976) did not find an increase in the rate of biodegradation in fertilized plots until a year after waste application. Dibble and Bartha (1979a) reported that excessive rates of mineral nutrient addition did not favor waste biodegradation. Atlas (1977) suggests that the best fertilizer for soil application is a form of readily usable nitrogen and phosphorus along with a form of slow release fertilizer to prevent leaching losses.

Thus, the present data and data reported in the literature indicates that additions of the proper amounts of selected nutrients can increase biodegradation, while excessive amounts provide no benefit. Most of the results have indicated that nitrogen is the most needed nutrient, and additions are dependent on the waste characteristics. Dibble and Bartha (1979b) found an optimum C:N ratio of 60:1 for their oily waste, while one of those considered here exhibited an optimum of 9:1 and the other 124:1. It would appear that optimum nutrient additions will need to be determined for each waste. Care must be also be taken, however, to avoid additions of excess nitrogen fertilizer which could contribute to leaching of nitrates.

Microbial Analysis

The results of microbial analysis of the waste and waste-amended Norwood soil following 180 days incubation at 40 C are shown in Table 15.

TABLE 15. MICROBIAL POPULATION IN THE NORWOOD SOIL 180 DAYS FOLLOWING WASTE APPLICATION OF DIFFERENT AMOUNTS OF TWO OIL WASTES.

Waste Applied	g. Hydroc./ 100g Soil	Total Viable Soil Bacteria CFU/g	Total Viable Hydrocarbon Utilizing bacteria	H.U.B./ x 100/ /TVH	Total Soil Fungi (CFU/g)	Hydrocarbon Utilizing Fungi (CFU/g)	Total Soil F/ H.U.F.
%		x 10^5	x 10^5	%	x 10^4	x 10^4	%
Refinery							
0	0	4.1	0.46	11	7.9	0.63	8
1	0.10	10.9	1.50	14	13.0	5.70	44
5	0.50	6.2	1.10	18	-	-	-
10	1.00	6.0	0.29	5	2.1	0.21	10
Petrochemical							
0	0	4.1	0.05	1	7.9	0.50	6
1	0.62	80.0	4.30	5	4.2	2.10	50
5	3.10	79.0	5.20	7	6.3	1.40	22
10	6.20	62.0	1.20	2	0.13	0.10	77
Refinery Waste		0.94	0.83	88	0.01	0.01	100
Petrochemical Waste		0.10	0.05	50	0.43	0.03	6

The addition of waste increased the number of total soil bacteria above the count in the unamended soil in all cases. The increase was most obvious with the petrochemical waste in which average counts ranged almost nine times greater than the population of the total soil bacteria in soils amended with the refinery waste. Both total soil bacteria and hydrocarbon utilizing bacteria were stimlated by the addition of oil waste as shown in Figures 19 and 20, but the effect was more evident in the case of the petrochemical waste. For both wastes, the numbers of soil bacteria were greater when 1% (wt/wt) of either waste was added to the soil. Additions of 5 and 10% of either waste resulted in slightly lower numbers. Hydrocarbon utilizing bacteria

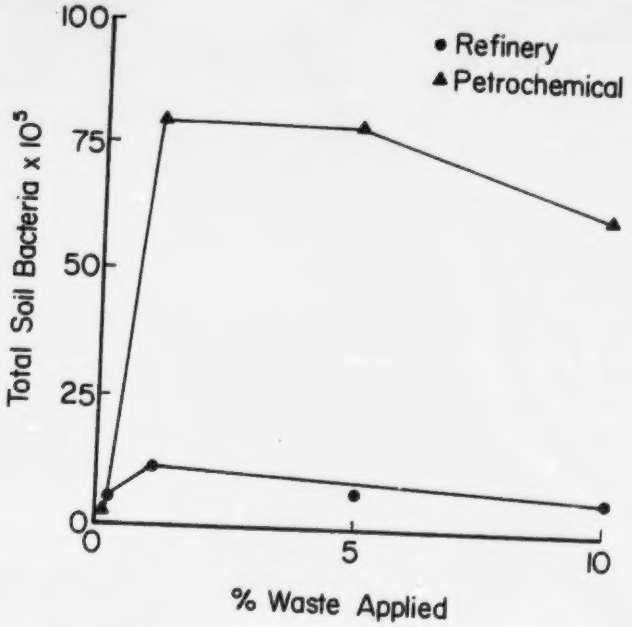


Figure 19. Total soil bacteria in Norwood soil amended with different amounts of both wastes after incubation at 40 C and 18% moisture for 180 days.

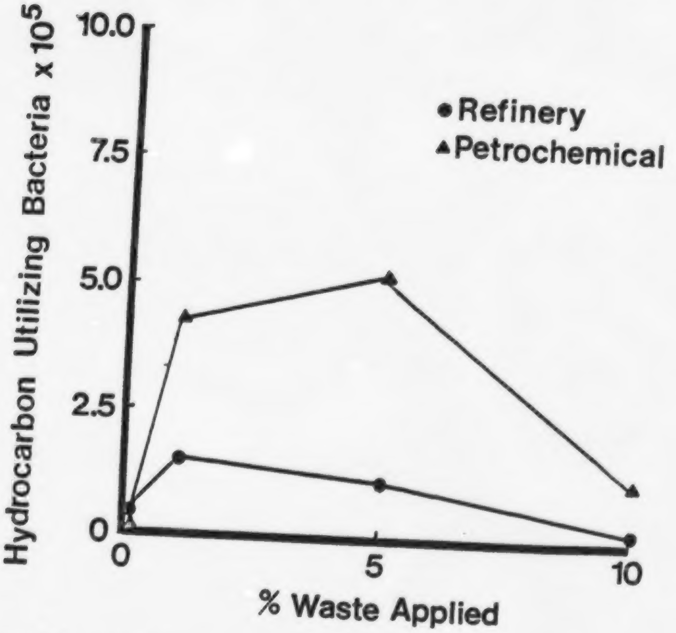


Figure 20. Total hydrocarbon utilizing bacteria in Norwood soil amended with different amounts of both wastes after incubation at 40 C and 18% moisture for 180 days.

accounted for 50 and 88% of the total soil bacteria isolated from the petrochemical and refinery wastes, respectively. In the unamended soil, 11% of the total soil bacteria were capable of using the refinery waste as a sole carbon source, while only 1% was able to utilize the petrochemical waste. In general, the addition of waste favored the increase in hydrocarbon utilizing bacteria over total soil bacteria. The 10% addition of the refinery waste reduced the population of hydrocarbon utilizing bacteria to a level below that of the unamended soil.

Plate counts were utilized to enumerate soil fungi. While total soil fungi in the waste were less than those found in the unamended soil, the hydrocarbon utilizing fungal population was of the same magnitude as those in the unamended soil. The results presented in Table 15 show that both the total soil fungi and the hydrocarbon utilizing fungi occurred in much lower numbers in the waste than in the unamended soil. As with the bacteria, the greatest numbers of hydrocarbon utilizing fungi were found when waste applications of 1% were added to the soil. Additions of 10% decrease the number of HCUF to below those found in the unamended soil. These data serve to indicate that both hydrocarbon utilizing bacteria and fungi are present in the unamended soil. Additions of either waste resulted in increased populations of both bacteria and fungi. The greatest numbers were found in general when 1% waste was added to the soil, while greater applications decreased the numbers below those found at 1%. Additions of 10% generally resulted in lower populations of fungi and bacteria than were found in the unamended soils, indicating the possibility of an inhibitory mechanism. Possible inhibitory mechanisms include the toxicity of certain waste components and a reduction in available water due to the hydrophobic nature of the wastes.

Half-Life Calculations:

Prior to the application of any waste material to land, it is necessary to determine to what extent the soil can be loaded with a particular waste without adversely affecting the environment. The enumeration of soil microbial populations indicated that applications greater than 5% of either waste reduced the size of the microbial population. In order to optimize biodegradation, the residual hydrocarbon level in the soil should be maintained below levels which can severely inhibit microbial activity. A comparison of microbial populations and degradation rates at the various application rates indicate that the optimum rate of waste application on a Norwood soil in a temperate climate falls between 5 and 10% (wt/wt) for both the refinery and the petrochemical wastes. These rates convert to approximately 1.12 x 10^5 and 2.24 x 10^5 kg of sludge per ha, respectively, assuming incorporation of waste into top 15 cm of soil.

The results presented in Table 16 illustrate the degradation rates for several waste fractions as evaluated by both cumulative CO_2 evolved and residual hydrocarbon extractions. These results indicate the slowest rate of degradation occurred for both wastes in the condensed ring fraction. Residual hydrocarbon extraction and CO_2 analysis exhibit a good correlation for the refinery waste, with the rates of degradation calculated to be 63 and 69% for the residual hydrocarbon and CO_2 analysis, respectively. After six months of incubation, the extraction of hydrocarbons from the soil and subsequent separation on a silica gel column revealed that 82% of the carbon applied in the condensed ring fraction could be recovered from the soil. Using an 18% degradation rate for a 180 day period, the half-life of the condensed ring fraction was calculated to be 500 days (Table 17).

TABLE 16. CHARACTERISTICS OF WASTE BEFORE AND AFTER 180 DAYS INCUBATION AT 30 C AT AN APPLICATION RATE OF 5% (WT/WT) TO A NORWOOD SOIL

		Extractable Hydrocarbons (mg)				
		Total	Petroleum Ether	Petroleum Ether: Dichloromethane	Dichloromethane	Cumulative CO_2 - C Evolved
Refinery Waste	Carbon applied	500	396	121	33	350
	Carbon residual	183	90	66	27	240
	% Carbon degraded	63	77	45	18	69
Petrochemical Waste	Carbon applied	3,100	1,953	1,085	62	2,100
	Carbon residual	2,060	1,188	827	45	310
	% Carbon degraded	34	39	24	27	15

The characteristics of the petrochemical waste after six months of soil incubation (Table 16) indicate that this waste was much less susceptible to microbial action than the refinery waste. These results also indicate that there is a poor correlation between the degradation rates calculated by residual carbon and CO_2 evolution. Only 34% of the

TABLE 17. HALF-LIFE OF ORGANIC SUBFRACTIONS OF BOTH WASTES

	Half-life (Days)				
	CO_2 - C Evolved	Extractable Hydrocarbons (Total)	Petroleum Ether (Saturate)	Petroleum Ether: Dichloromethane (Aromatic)	Dichloromethane (Condensed Ring)
Refinery Waste	130	143	116	119	500
Petroleum Waste	600	264	231	375	333

applied carbon could be recovered by solvent extraction after the six month incubation period, while 15% of the applied carbon was recovered as evolved carbon dioxide. The differences between the calculated degradation rates may have resulted from the inability of solvent extraction to recover carbon which had been incorporated into the microbial cell mass.

The half-life calculations for the subfractions of the organic fraction (Table 17) indicate that at a 5% application rate, 333 days would be required to degrade half the applied condensed ring fraction while only 231 days would be required to degrade half the applied saturate fraction. The half-lives calculated for the total extractable or the carbon evolved as CO_2 were 264 days and 600 days, respectively. The most restrictive half-life calculated by these methods was that which was calculated for evolved carbon dioxide. If the half-life was used as the basis for land treatment, 5 to 10% of the petrochemical waste would be applied once every 600 days. This application rate should only serve as a guideline for field applciations, and the rate may be adjusted based on field verification studies.

SUMMARY

Parameters studied included soil texture, soil moisture, mineral nutrient amendments, application rates, application frequency, and temperature. Maximum degradation rates were achieved with the Norwood sandy clay at a temperature of 30 C. The greatest rate of biodegradation per unit of waste applied occurred when small applications were made at frequent intervals. Addition of mineral nutrients effectively increased biodegradation rates of both the refinery and the petrochemical sludges. The soil microcosm was stimulated by small applications of waste, but reduced numbers of microorganisms were found when the application rates exceeded 5 g/100g of soil for either sludge. Thus, a comparison of degradation rate and the microbial population indicates that the optimum application rate for both wastes is 5% to 10% by weight (1.1×10^4 to 2.2×10^4 kg/ha).

SECTION 6

LABORATORY MOBILITY STUDIES ON WATER SOLUBLE CONSTITUENTS

INTRODUCTION

Land treatment, which involves using the surface soil as a treatment and disposal medium, has been practiced by the petrochemical industry for handling process sludges. However, the lack of systematic study or monitoring of past or present sites has limited the knowledge of the active mechanisms within the soil. Information is needed on site selection, waste characteristics, optimum soil and climatic conditions for degradation of organic constituents, application rates and scheduling, decomposition products, and the potential for ground water contamination.

In particular, the objectives of this research are as follows:

(1) To identify compounds or classes of compounds in a representative API oil-water separator sludge which are water soluble and/or mobile in soils.

(2) To utilize laboratory studies to compare relative mobilities of solubilized constituents in soil.

(3) To elicit mechanisms which are active in leaching or immobilizing these compounds in soils.

(4) To evaluate the hazard to groundwater of leached components from these refining wastes.

MOVEMENT OF OIL IN SOILS

Several modes of transport can be described for the movement of oil or petroleum compounds through the soil. As a continuous phase, oil can move as a fluid governed by the same parameters as those which determine soil water movement. Alternatively, water soluble or miscible compounds can be physically transported by soil water. Small magnitude movement might also be due to diffusion, although not to a significant level in terms of leaching hazards.

Migration of Oil

The behavior of oil moving as a continuous phase in soil is fairly well understood; however, data from oily waste disposal sites indicate that, at low application rates, little migration occurs. In a study of three disposal sites by Raymond *et al*. (1976), no significant movement of oil was seen in leachate waters. Stearns *et al*. (1977b) reported one case of migration of oil under unfavorable circumstances at a Southern California location where waste oil was deposited on a sand overlying a fluctuating perched water table.

Cases of Minimal Leaching

Most of the information on leaching of petroleum waste through soils has resulted from field observations of active oil spills or sludge disposal sites by means of test cores or monitoring wells. Current findings on leaching are mixed and inconclusive partly because analyses are usually on the basis of oil and grease content and total organic carbon (TOC). Several monitoring programs have detected no significant leaching of organic carbon. Huddleston and Meyers (1978) land treated API separator sludge, 5% (w/w) oil in silty clay loam with 1% organic matter, and practiced an accepted management scheme. After 10 months, no significant leaching, as determined by TOC analysis was found below the mixing depth. However, climatic factors were not addressed in the paper. In a case at Tulsa, Oklahoma where a 1:1 oily sludge:biosludge mixture was applied, almost no contamination was found at well points after 14 months (Weldon, 1978). In a second location, no oil was found at greater than 12.5 cm below the zone of mixing, although the water table which fluctuated near the surface apparently caused some pollution of test wells by soluble hydrocarbons. Leachate samples taken below a 60 cm mixing depth by Kincannon (1972) showed no evidence of oil movement from a sandy clay loam. Inconclusive data from an operational land treatment location by Lewis (1977) found well point leachate water comparable to a nearby creek as determined by analysis of oil and grease and TOC. However, there was no background sampling, and the creek is located within a dense petroleum refining area. Finally, arid regions should present little chance of leaching as evidenced by a Little Mountain, Utah waste disposal operation where climate and lack of groundwater have prevented any detectable hydrocarbon contamination (Stearns *et al*., 1977b).

Cases of Significant Leaching

Several petroleum leaching studies have reported movement of water soluble components. Francke and Clark (1974), analyzing for TOC below 75 cm, found average losses of 7.1, 14.6, and 91.0 $\mu g\text{-}ml^{-1}$ for control, oil treated plots, and coolant treated plots, respectively. Based on calculations for a 57 day test period, 0.064% of the coolant and 0.049% of the oil constituents were lost to percolation. In addition, elevated TOC levels were observed in control plots, possibly as a result of lateral contamination. The authors also observed percolate water from 2.7 m test wells containing from 6 to 33 ppm TOC which was not considered significant. However, there was no attempt to determine the origin of the compounds making up the TOC. In a study of oil behavior in soils by Raymond *et al*. (1976), leachate waters were analyzed for oil and grease, then extracted to determine water soluble organics. Results suggested significant movement of soluble organics. Also of note, the analyses indicated a similarity in compounds present between controls and plots receiving oil, which may suggest interplot migration of oil. In laboratory work on a sand and on undisturbed cores where oil had been spilled, Duffy *et al*. (1977) observed significant leachate contamination in both cases. Concentrations in the leachate from the sand, to which crude oil was added to a depth of 1.72 cm, still exceeded 0.4 ppm oil after 5300 cm of water was applied. Soil core leachate ranged from 0.4 to 12.6 ppm oil.

General Behavior

Several general observations of oil behavior in soil bear directly on any assessment of groundwater pollution hazards. In conjunction with attenuation by degradation, oil composition changes with depth below a spill or sludge application. Plice (1948) observed that when oil enters the soil as a phase, there is a filtering effect where high molecular weight, viscous compounds are held near the surface while the lighter fractions penetrate deeper. Another separation which can be observed is that while oil concentrations tend to decrease with depth, the aromatic fraction moves more selectively such that it constitutes an increasing fraction of the oil (Duffy *et al*., 1977; Weldon, 1978). Once oil fractions reach deeper anaerobic layers, degradation has been shown to be extremely slow. Duffy *et al*. (1977), using the ratio of isoprenoids to the preferentially utilized n-alkanes, found little oil decomposition and in one case showed no significant degradation in anaerobic zones after 13 years. Duffy *et al*. (1977) further cited data showing that, once in the groundwater, leached oil is persistent up to 100 years or more, therefore posing a long-term threat. Studies by Kappeler and Wuhrmann (1978) have indicated that various microorganisms, such as some isolates of the genus *Pseudomonas*, capable of utilizing soluble petroleum compounds are found in groundwater; however, degradation is highly dependent upon oxygen and possibly nitrogen, which may be lacking in groundwater.

The Water Soluble Fraction

The distribution of oil with depth in soil reflects the composition of the water soluble fraction. Guard *et al*. (1975) indicated that little had been done on the identification of water solubles in oils. However, several recent publications add to the knowledge of water soluble petroleum compounds. Nathwani and Phillips (1977) found that the most soluble constituents were the lower alkanes and aromatics, with equilibrium concentrations on the order of 8 ppm. Crude oil and kerosene extracts by Boylan and Tripp (1971) yielded almost all aromatics in the low boiling range, 80 to 262 C; however, an envelope of high boiling aromatics was also present. Table 18 lists compounds or classes of compounds found by several investigators. Notably, these extractions were for crude or refined petroleum, and no data are available for API separator sludge. Whatever the nature of the material, the water soluble fraction possesses the greatest potential for leaching and consequent groundwater contamination.

MOBILITY RESEARCH USING PESTICIDES

Despite the paucity of leaching information concerning petroleum compounds, intensive research on organic pesticides in recent years has developed a good understanding of physical, chemical, and biological interactions within soils. Studies of pesticides have the advantage that the compounds of interest are known and that the compounds may be radioisotopically labeled. Principles and parameters established through pesticide research should be generally applicable to the petrochemical water soluble fraction. Many pesticides are in fact hydrocarbon derivatives and should exhibit similar behavior in soils.

TABLE 18. WATER SOLUBLE FRACTIONS FROM VARIOUS PETROLEUM STOCKS

Crude oil†	Crude, fuel, and crankcase oils§	Gas oil¶	Bunker fuel oil#
benzene	benzenes	methylbenzenes	naphthalene
alkylated benzenes	naphthalenes	ethylbenzenes	methylnaphthalenes
naphthalene	phenols	naphthalenes	phenol
alkylated naphthalene	biphenyls	methylnaphthalenes	o- and p-cresol
monomethyl-naphthalene	indans	tetrahydronaphthalene	xylenols
tetrahydro-naphthalene	tetralins	propylbenzenes	acetophenone
phenol	anilenes	butylbenzenes	2-phenyl-2-propanol
m- or p-cresol	quinolenes	ethyl-methylbenzenes	
low m.w. paraffins	indoles	indan	
high boiling unresolved	benzothiophes		
	phthalides		
	benzaldehydes		
	aromatic ketones		

† Duffy et al. (1977) and Larson and Weston (1976)
§ Winters and Parker (1977)
¶ Kappeler and Wuhrmann (1978)
# Guard et al. (1975)

Soil as a Chromatographic Column

In one model of organic pesticide movement, soil was treated as a chromatographic column where the soil minerals were the inert support, organic matter the active stationary phase, and water and air are the carrier phase (Lambert *et al*., 1965). Theoretical concepts applied to a homogeneous soil system allowed calculated mobilities which closely matched laboratory and field observation. From such a treatment of the soil system, several factors which affect chromatographic separations may be summoned to explain movement of organics in soils. Parameters of importance include the nature and concentration of the stationary phase, particle or aggregate size of the support, activities of the support, polarity and structure of the sample compound, and carrier flux.

Adsorption and Organic Matter

Observations by many investigators suggest that organic matter content of soils is one of the most influential parameters on the mobility of organic compounds. In their review of adsorption and desorption of organic pesticides, Bailey and White (1964) showed leachability in the order of organic soils < clay soils < coarse soils. Their review continued by noting that organic matter content and cation exchange capacity (CEC) are correlated between themselves and are highly positively correlated with adsorption. Organic matter was the single best predictor of adsorption, accounting for up to 77% of observed variations. Nathwani and Phillips (1977), studying the adsorption and desorption of selected hydrocarbons on soils, found that organic matter accounted for most of the observed differences. Desorption ranged from 85% down to 45% for soils ranging from 1 to 16% organic matter content, respectively. Research into the movement and sorption of pesticides by Lambert *et al*. (1965) also showed that organic matter and water content accounted for practically all variations. Soil thin-layer chromatography (soil TLC) investigations by Helling (1971b) demonstrated that in most cases removal of organic matter increases mobility of pesticides, except where preferential adsorption by clay predominates.

Mobility and Soil Structure

Column leaching studies have demonstrated the effect of soil structure on pesticide mobility. Dekkers and Barbera (1977) proposed that kinetic effects due to soil structure have a greater influence on herbicide transport than soil adsorption capacity. When herbicide was mixed in the top layer of soil columns prior to water application, herbicide movement was less than that estimated by assuming adsorption-desorption equilibrium. Larger aggregates seemed to decrease the mean movement of herbicides due to faster water movement which allowed less time for solute transport to the liquid phase. Computations by Leistra and Dekkers (1977) showed that for slower adsorption-desorption kinetics, there is a lag in pesticide leaching compared to the commonly assumed instantaneous equilibrium. Within soil aggregates, adsorption time is increased as the diffusion rate limits solid to liquid transfer (Dekkers and Barbera, 1977). Conversely, pesticides have been found to leach further when they start in solution (Leistra and Dekkers, 1977). Investigations by Davidson and Chang (1972) illustrated that Picloram applied in solution exhibited lower adsorption or greater mobility, as aggregate size increased.

Effects of Soil pH

Soil reaction has been shown by observation to affect the mobility of some compounds. Soil TLC experiments on pesticides by Helling (1971c) showed that only organic acids are significantly affected by soil pH. The dissociation constant, pK_a, is a key factor in mobility such that as pH deviates from the pK_a, adsorption of organic acids decreases and mobility increases (Helling, 1971b). A review by Bailey and White (1964) on adsorption-desorption of organics also pointed out this relationship of adsorption and pH. Bailey _et al_. (1968) performed adsorption studies on 23 pesticides in montmorillonite systems and observed greater adsorption on acid H-montmorillonite than on near neutral Na-Montmorillonite. The investigators concluded that within a family or analog series of pesticides, the degree of adsorption is controlled by and inversely related to water solubility, while between families the major factor is the dissociation constant.

Soil Water Flux

Solvent flux has also been found to markedly influence the movement of organic pesticides in soils. By varying the solvent flux by physical and chemical means, Helling (1971a) used soil TLC to determine the correlation between flux and relative mobility expressed as R_F. Mobility of nonionic pesticides was directly correlated with water flux and inversely related to clay content, organic matter, and CEC (Helling, 1971c). Davidson and Chang (1972), working with soil columns, found that the mobility of Picloram was influenced by water velocity. Displacement was seen to decrease as the average pore water velocity was reduced from 5.8 to 0.59 cm-hr^{-1}.

SUMMARY OF LEACHING INFORMATION

A review of current knowledge of mobility and leaching of oils, API oil-water separator sludge in particular, in soils points to the scarcity of available information. Leachate sampling of field locations almost exclusively accounts for existing data. In many of these cases, results are inconclusive because of failure to obtain background levels before sludge application, interplot migration of contaminants into control plots, or indeterminate field conditions. Once the leachate is sampled, analyses have usually included only inorganic, oil and grease, and total organic carbon (TOC). Further analyses are essential to determine organic compounds or classes of compounds being leached, their relative mobilities, and their potential for groundwater contamination. Finally, the limited number of investigations on water soluble petroleum fractions have considered only crude or refined petroleum while no one reports water solubles from petrochemical waste slduges.

MATERIALS AND METHODS

Design

A twofold approach, consisting of soil thin-layer chromatography (soil TLC) and soil column experiments, was implemented to assess the leachability of the selected waste sludge. Water soluble fractions (WSF) of the waste were applied to the soil TLC plates while the original sludge material was applied to soil columns. After elution with deionized water, gas-liquid chromatography (GLC) was utilized to fingerprint the mobile waste constituents. These constituents were then identified by means of a gas chromatograph interfaced with a mass spectrometer (GC-MS). A simple flow chart (Figure 21) illustrates the experimental design.

EXPERIMENTAL MATERIALS

Soils

Three of the four soils utilized in the phytotoxicity study were used in this study. They were the Bastrop sandy loam, Nacogdoches clay, and Norwood silt loam soils and

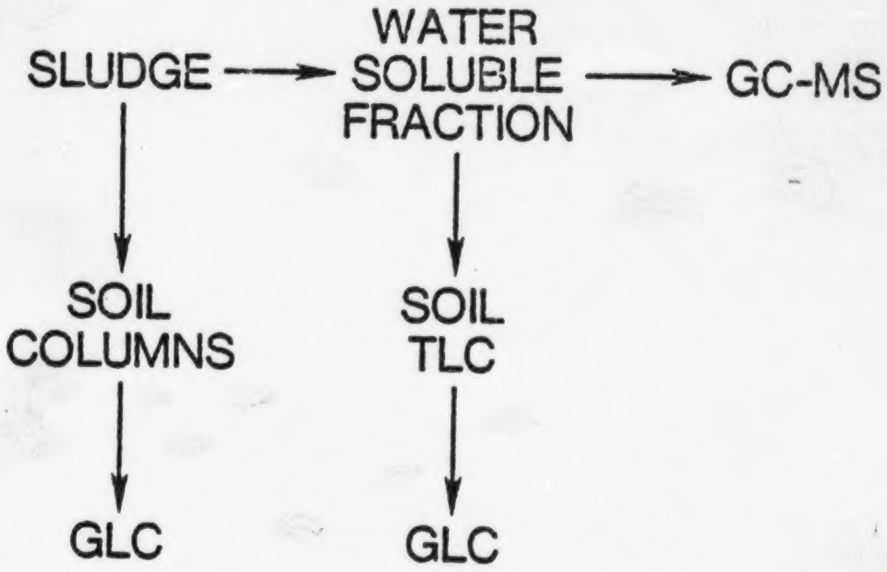


Figure 21. Experimental methods flow chart.

their native properties are given in Table 1. In order to conform to the methods of Helling and Turner (1968) for soil TLC, the soils were ground and passed through a 250 m sieve to remove medium to coarse sand for all analyses. Table 19 describes the sieved soils.

Waste

The waste material was an API oil-water separator sludge from the petroleum refining industry. A survey of refiners revealed that this class of waste could vary widely depending upon crude stocks, refinery end products, and plant equipment and management. The sludge used in this study was obtained from a refinery producing primarily fuels and lubricants. An analysis of the sludge is summarized in Table 2.

WASTE EXTRACTION

Water soluble fractions of the waste were prepared by adapting the procedures of Boylan and Tripp (1971) and Winters and Parker (1977). Extracting solutions were 10^{-3} N NaOH and 10^{-3} N HCl which represent extremes of possible soil solution pH. Slow stirring of one part sludge to ten parts extractant (w/w) for 24 hours dissolved the WSF while

TABLE 19. SIEVED SOIL PROPERTIES

Series	Classification	USDA Texture	% Organic Carbon	pH	CEC (meq/100g)
Bastrop	Fine-loamy, mixed thermic Udic Paleustalfs	SaL	1.17	6.6	16.1
Nacogdoches	Fine, kaolinitic, thermic Rhodic Paleudalfs	CL	0.53	5.8	20.9
Norwood	Fine, silty, mixed (calcareous) thermic Typic Udifluvents	L	0.47	7.7	14.5

preventing formation of an emulsion. The mixtures were allowed to stand for at least 24 hours until the light oil fraction floated to the surface while the denser materials settled. The aqueous phase with the WSF was siphoned and filtered through Whatman #42 filter paper. Solutions were either acidified with HCl to pH 2 or adjusted with NaOH to pH 12 in order to facilitate partitioning of the organics into an organic solvent. Following transfer to a separatory funnel, the WSF was partitioned into benzene with 1:1 benzene:acetone. Partitioning of the acidified solutions yielded the organic acids, neutrals, and phenols. Neutrals and bases were partitioned into the benzene from the pH 12 solution.

Benzene was the solvent of choice based on a review of previous studies of WSF methodology and on knowledge of the API sludge characteristics. Extraction of water soluble compounds by Guard et al. (1975) and by Larson and Weston (1976) were performed using chloroform. However, comparisons of hexane, chloroform, and benzene for the recovery of petroleum compounds from sediments showed that benzene was most efficient (Walker et al., 1975). In addition, Winters and Parker (1977) employed benzene as their extractant for dissolved oils. All of these investigations of the WSF of petroleum also revealed that mostly aromatic compounds were present. Aromatics are more readily soluble in benzene. API separator sludge should be depleted of lighter aliphatics due to the refining process, and, therefore, aromatics should account for a larger proportion of the soluble waste organics.

SOIL THIN-LAYER CHROMATOGRAPHY

Mobility of components of the WSF was determined by utilizing the soil TLC technique of Helling and Tuner (1968). A slurry of soil and water was applied to 20 x 20 cm glass plates such that the soil layer thickness was 500 _m. The air dried soil plates were scribed at 12 cm, and about 10 mg of concentrated sample material was applied as a streak at 2 cm for a development distance of 10 cm. After allowing sufficient time for evaporation of the solvent, the plates were developed at an angle of 20° from the vertical with deionized water as the mobile phase and were removed from the developing tank when the wetting front reached the scribed line. Upon air drying, successive 1 cm zones of soil were removed from the plates, placed in disposable pipettes, and eluted with 10 ml of benzene to extract any waste components present. Blank soil plates were likewise developed to determine background values. Extracts of both treated and blank plates were concentrated to 10 _1 final volume for GLC fingerprinting.

SOIL COLUMNS

Column leaching studies were performed by packing sieved soil into 0.44 m x 2.54 cm ID glass columns having fritted glass bases (Figure 22). Soil was added by layers, tamped, and scarified in order to achieve a consistent bulk density approaching common field values. API separator sludge was mixed with the top 2 cm of soil at a rate equal to 5% (w/w) of the entire soil column, which is the optimum application rate for field soils as determined by microbial respiration studies. The soil was leached with three pore volumes of deionized water, and the leachate was collected in three corresponding fractions. Due to the low permeability of the surface soil-sludge mixture, suction was applied to speed the leaching process. Organics in the leachate were partitioned into benzene as in the extraction of the WSF and analyzed by GLC for waste components. One control column and two columns with waste were tested for each soil. Table 20 describes the soil column parameters.

Effective porosity as shown is defined as porosity minus percent of air filled pores. Since the soil volume was 100 cm^3, effective porosity was easily determined by adding 43.4 ml of deionized water, measuring the leachate volume

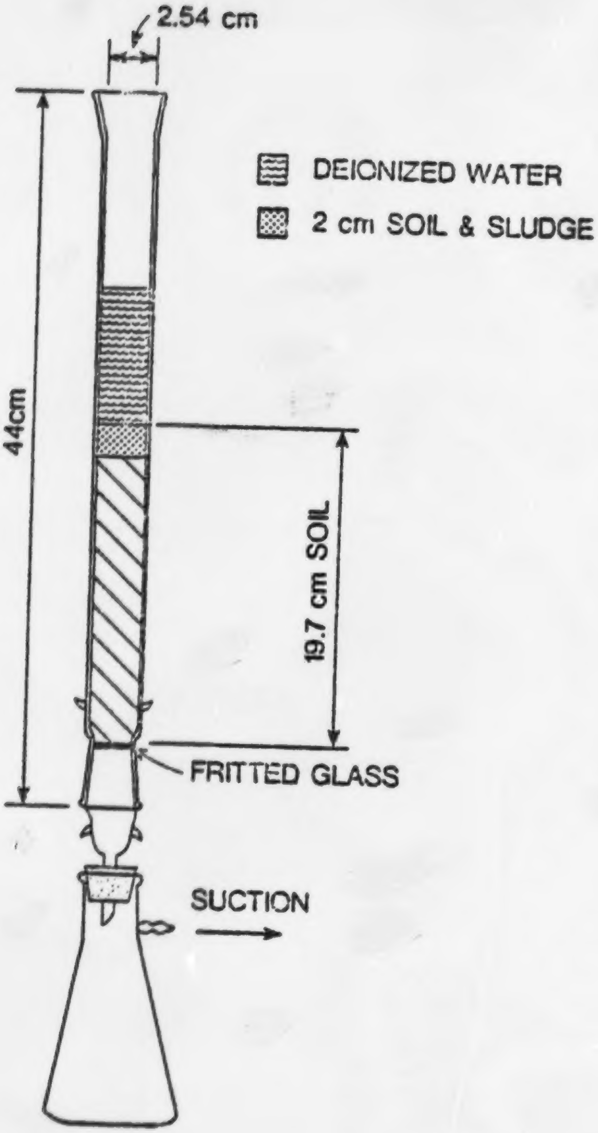

2.54 cm
DEIONIZED WATER
2 cm SOIL & SLUDGE
44cm
19.7 cm SOIL
FRITTED GLASS
SUCTION

Figure 22. Soil column configuration.

when the water level reached the soil surface, and applying the following equation:

$$EP = P + \theta_{vi} \times 100\% - L$$

where:

EP = effective porosity (%)
P = porosity (%)
θ_{vi} = initial soil volumetric water content
L = leachate volume expressed as percent of bulk soil volume.

TABLE 20. SOIL COLUMN PARAMETERS

Soil	Bulk Density g cm^{-3}	O.D. Soil Weight g	Soil Depth cm	Waste Added g	Porosity %	Effective Porosity %
Bastrop	1.5	150.0	19.7	7.5	43.4	40.0
Nacogdoches	1.5	150.0	19.7	7.5	43.4	40.6
Norwood	1.5	150.0	19.7	7.5	43.4	42.2

ANALYSIS TECHNIQUES

To monitor the mobile waste components, GLC was employed to fingerprint the WSF and the extracts from the soil TLC plates and from the soil columns. A Barber Colman Model 5360 pesticide analyzer was equipped with a flame ionization detector (FID) and a 1.8 m x 4 mm ID glass column packed with 5% Carbowax 20M on 100/120 mesh Supelcoport. The carrier gas was prepurified nitrogen at a flow rate of 60 cm^3-min^{-1} and compressed air at 300 cm^3-min^{-1}. Inlet and detector temperatures were set at 250 and 290 C, respectively, while column temperatures were manually programmed between 100 and 200 C. As internal standards on the GLC scans, about 100 ng each of anthracene, which elute first, and 1, 2, 3, 4, 5, 6, 7, 8 octahydroanthracene were coinjected with each sample.

Fractionation and identification of leachable compounds was performed by gas chromatography-mass spectrometry

(GC-MS) using the MS as the detector. Carrier gas flow was 30 cm^3-min^{-1} through a 1.8 m x 3.2 mm ID glass column packed with 5% Carbowax 20M on 100/120 mesh Gaschrom Q. Column temperatures were programmed from 100 to 200 C at 2 deg-min . The mass spectrometer was adjusted to detect molecular weights between 60 and 500, and output was displayed as a bar graph for each compound along with a GLC scan of the sample.

RESULTS AND DISCUSSION

The logical sequence which was developed for evaluation of leachate hazards proceeded from the extraction and analysis of the sludge through soil mobility screening. An assessment of the experimental results was supplemented with published information on identifiable compounds. Since little methodology had been previously designed for such an evaluation, techniques were synthesized from published work and from the experimental design considerations.

THE WATER SOLUBLE FRACTION

The extractions of the water soluble fraction yielded samples for use in soil TLC and for chemical analysis. General qualitative observations and chemical analysis results revealed that 10^{-3}N NaOH and 10^{-3}N HCl extracts were of similar composition. Additionally, partitioning at pH 2 into benzene removed the greater variety and concentrations of hydrocarbons from the water phase, inclusive of all of the identifiable compounds partitioned from the pH 12 adjusted sludge extract. Based on this information, only the 10^{-3}N NaOH extracts adjusted to pH 2 were employed in soil TLC experiments.

General Properties

Following the 48 hour stir/settle-infiltration period, pH of the solutions averaged 7.7 before partitioning into the organic solvent (Table 21).

There was no significant pH difference between NaOH and HCl extracts at the 5% level in a pooled t-test with six degrees of freedom. The absence of an extractant effect suggests that the sludge system is strongly buffered and that further extractions could be accomplished using deionized water. However, for all soil TLC applications, NaOH extracts were employed. Equilibrium concentrations of soluble hydrocarbons in the water were determined

TABLE 21. SOLUTION pH FOR 10^{-3}N HCl AND 10^{-3}N NaOH EXTRACTS OF AN API SEPARATOR SLUDGE

Extractant	PH					Mean	SD
	1	2	3	4	5		
NaOH	7.7	7.6	7.3	7.5	7.8	7.6	0.19
HCl	7.9	7.9	7.6	-	-	7.8	0.17

gravimetrically and averaged 24 ppm for three of the five extracts used in soil TLC. Duffy *et al*. (1977) cited references of human detection limits of some hydrocarbons to be as low as 1 ppb. If attenuation by degradation or adsorption does not occur, 24 ppm soluble hydrocarbons may at the least render the groundwater disagreeable for consumption if not toxic.

Chemical Analysis

Since dilute acid, deionized water, and dilute base had no effect on extractions as seen by the filtered aqueous phase pH, any remaining differences between extracts would have been a function of solution pH adjustments before partitioning into benzene. Acids, neutrals, and phenols were partitioned by adjustment to pH 2. Neutrals and bases were partitioned by adjustment to pH 12.0. In another instance, a pH 7.6 aqueous phase was partitioned directly. Table 22 lists the soluble constituents, as determined by GC-MS, in the order of increasing retention time on a Carbowax 20M column. The pH 2 and 7.6 extracts were essentially the same and included all of the compounds identified in the pH 12 extracts. Based on comparisons of the three fractions, adjustment of pH 2 was chosen to be inclusive of most water soluble compounds. Consequently, all soil TLC applications received pH 2 extracts.

Notable in the water soluble fraction are phenols, napthalenes, and dibutylphthalates, which ae listed as hazardous constituents by EPA in Appendix 8 of 40 CFR, Part 261, 1980. Substances included in the decree were considered by the U.S. EPA to be hazardous based on toxicity

TABLE 22. WATER SOLUBLE FRACTION OF AN API OIL-WATER SEPARATOR SLUDGE. THE THREE EXAMPLES WERE ADJUSTED WITH HCl, NOT ADJUSTED, AND ADJUSTED WITH NaOH, RESPECTIVELY, BEFORE PARTITIONING INTO BENZENE

Retention time (min)	Molecular weight	pH 2	pH 7.6	pH 12
8.6	128	naphthalene		
10.9	134		2,3-benzothiophene	
12.5	142	n-methylnaphthalene	n-methylnaphthalene	
15.2	148	methylbenzothiophene	methylbenzothiophene	
19.0	156	n,n'-dimethylnaphthalene	n,n'-dimethylnaphthalene	
19.0	132	indan-1-one	indan-1-one	indan-1-one
20.2	94	phenol		
20.7	108	cresol		
22.7	170	trimethylnaphthalene	trimethylnaphthalene	
22.7	154	acenaphthene	acenaphthene	
22.7	134	dimethylbenzaldehyde	dimethylbenzaldehyde	dimethylbenzaldehyde
23.7	122	xylenol	xylenol	
26.6	122	methyl p-cresyl ether		
27.9	136		methyl-ethyl phenol	

TABLE 22. (CONTINUED)

Retention time (min)	Molecular weight	pH 2	pH 7.6	pH 12
28.5	168		n-methyl-biphenyl	
29.6	136	trimethyl-phenol	trimethyl-phenol	trimethyl-phenol
43.9	178		phenanthrene	
47.7	278	dibutyl phthalate	dibutyl phthalate	dibutyl phthalate
64.5	167	carbazole		carbazole
64.5	181	methylcarbazole		methylcarbazole
65.0	390		di-2-ethylhexyl-phthalate	di-2-ethylhexyl-phthalate
70.9	390		bis-(oct-n-yl)-phthalate	bis-(oct-n-yl)-phthalate

and environmental occurrence.

MOBILITY OF WASTE COMPONENTS THROUGH SOILS

Of the two techniques employed for assessing mobility, soil TLC more satisfactorily characterized soil interactions. Methodological difficulties with the column leachate extractions forestalled any conclusive appraisal of hydrocarbon leaching from the soil columns.

Determination by Soil TLC

Mobility of a given substance on soil TLC has been expressed by a relative measure R_F. A definition of R_F is the frontal movement, in centimeters, of the compound of interest divided by the distance, in centimeters, traversed by the wetting front (Helling and Turner, 1968). Since the wetting front moved 10 cm in these experiments, R_f values can be read easily by dividing frontal movement by 10. Such a measure, however, did not detect any significant differences between soils due to the consistent R_F values of 1.0. Control plates also revealed no detectable background or interferences from soil organic matter. Soil TLC was utilized as a semi-quantitative technique insofar as there was no attempt to extrapolate to the field the concentrations of water solubles to be expected in the leachate.

The general mobility patterns of the WSF can be visualized on a composite of four selected GLC scans from a soil TLC plate. Distributions of peak height for the three replicate plates of each soil were similar; therefore, one representative soil TLC plate is illustrated for each soil (Figures 23, 24, and 25). The Carbowax 20M is a moderately polar liquid phase such that retention time is a function of molecular weights within families of compounds and a function of polarity between families. Except for the phthalates and carbazoles which eluted at 200 C, the identified compounds in the WSF eluted at 150 C and at retention times between 30 and 90 minutes. The order of elution was the same as for the GC-MS data. By the general distribution of peak heights versus distance on soil TLC, all of the WSF is mobile with R_F values of 1.0 on all three soils, and the soluble compounds move similarly as a group. Summing the peak heights for compounds eluting at 150 C and averaging the replicates for each soil illustrates the bulk mobility pattern of the WSF (Figure 26).

For a more specific examination of mobility, five of the more abundant WSF components merit closer attention. As identified by gas chromatography-mass spectrometry, the compounds are n-methylnaphthalene, coeluting dimethyl-naphthalene and indan-1-one, and coeluting trimethyl-naphthalene and acenaphthene, respectively labeled D, G, and K in Figures 23 to 25. Comparison of their mobility patterns (Figures 27, 28, and 29) reveals several important relationships. First, an R_F of 1.0 for all of the compounds on all soils reflects the general trends as seen in the composite of WSF mobility. Although slight differences occurred between soils in some cases, no systematic soil effect was evident in terms of soil parameters. The R_F of a slightly to moderately mobile substance would be expected to reflect soil properties (Helling, 1971a); however, the extreme movement of the WSF accounted for a consistent response regardless of soil parameters.

Some differences between the mobility of n-methyl-, dimenthyl-, and trimethylnaphthalene were observed. Retardation of movement coincided with increasing polarity and molecular weight such that the order of movement was n-methyl > dimethyl > trimethyl. This behavior was analogous to elution from the Carbowax column, likening the soils to the chromatographic model of Lambert _et al_. (1965). Dibutyl phthalate was minimally transported and its distribution reflects its lower water solubility (Figure 30).

Anaomalous Soil TLC Patterns

A notable feature of the soil TLC results is the anomalously large concentration of sample at the origin, followed by minimal concentrations in zones 2 through 4 and by increasing concentrations through zone 10. Such a pattern is a typical of the common elution patterns and breakthrough curves for ionic species in soils. Similar distributions have been observed in studies of ^{14}C-labeled pesticide movement (C.S. Helling, personal communication), and although some of the strong origin spots were attributable to immobile impurities in the pesticides, several of the pesticide results could not be interpreted.

One plausible mechanism is derived from knowledge of the adsorption-desorption of organic chemicals on activated charcoal (A. R. Hanks, personal communication) as used in industrial dosimeters. Upon loading of readily accessible adsorption sites by an organic chemical, the microstructure of the charcoal was altered so that additional sites became

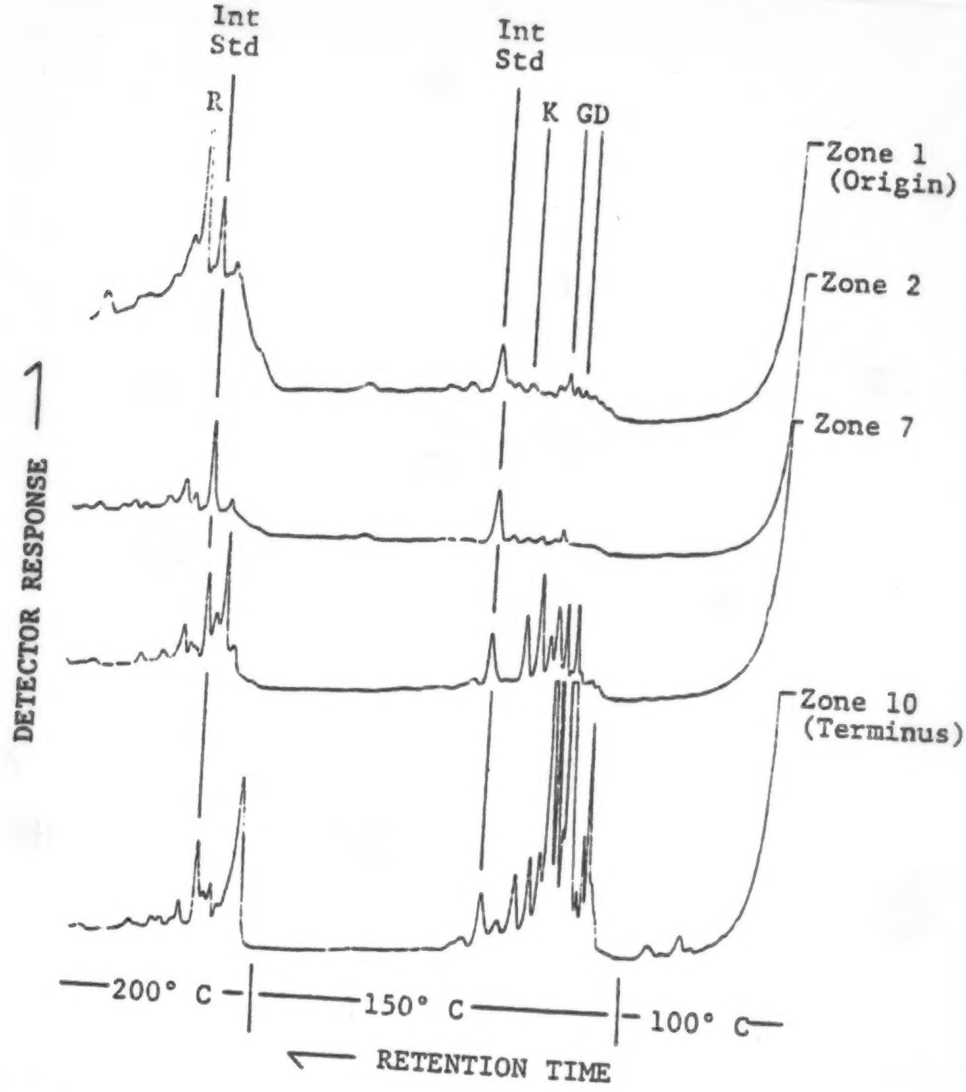


Figure 23. GLC visualization of soil TLC mobility distributions for the Bastrop series.

available for adsorption. In a soil system, these less accessible sites would include the interlayer spaces of silicate clay minerals. Benzene could act to alter the soil

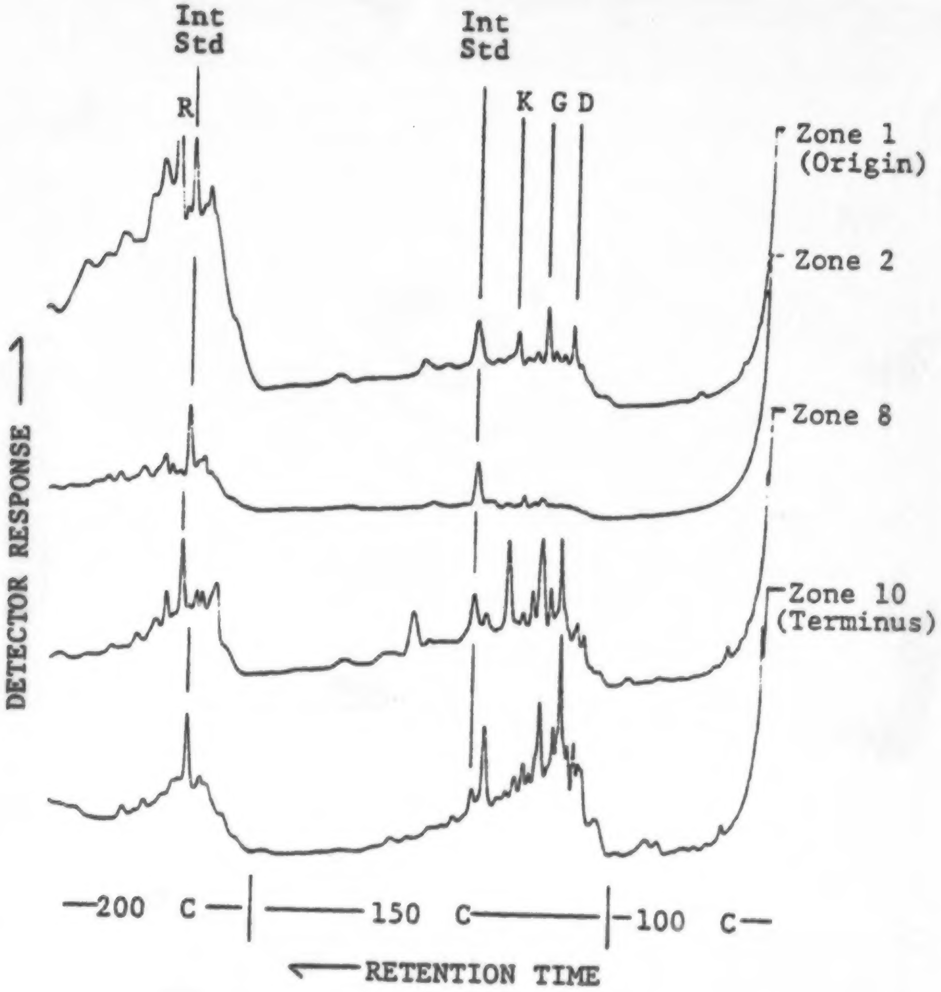


Figure 24. GLC visualization of soil TLC mobility distributions for the Nacogdoches series.

properties by this mechanism and increased adsorption of the WSF. Evaporation of the benzene might partially close these sites to the water used in developing a the soil TLC plates. Subsequent extraction of the origin streak with benzene could reverse the process and desorb the more tightly bound portion of the WSF. Mobility information in this case is valid since the mobile fraction of the WSF interacts with the normally available adsorption sites in the absence of benzene. Verification of the proposed mechanism could be accomplished through a series of batch adsorption-desorption tests utilizing other solvents.

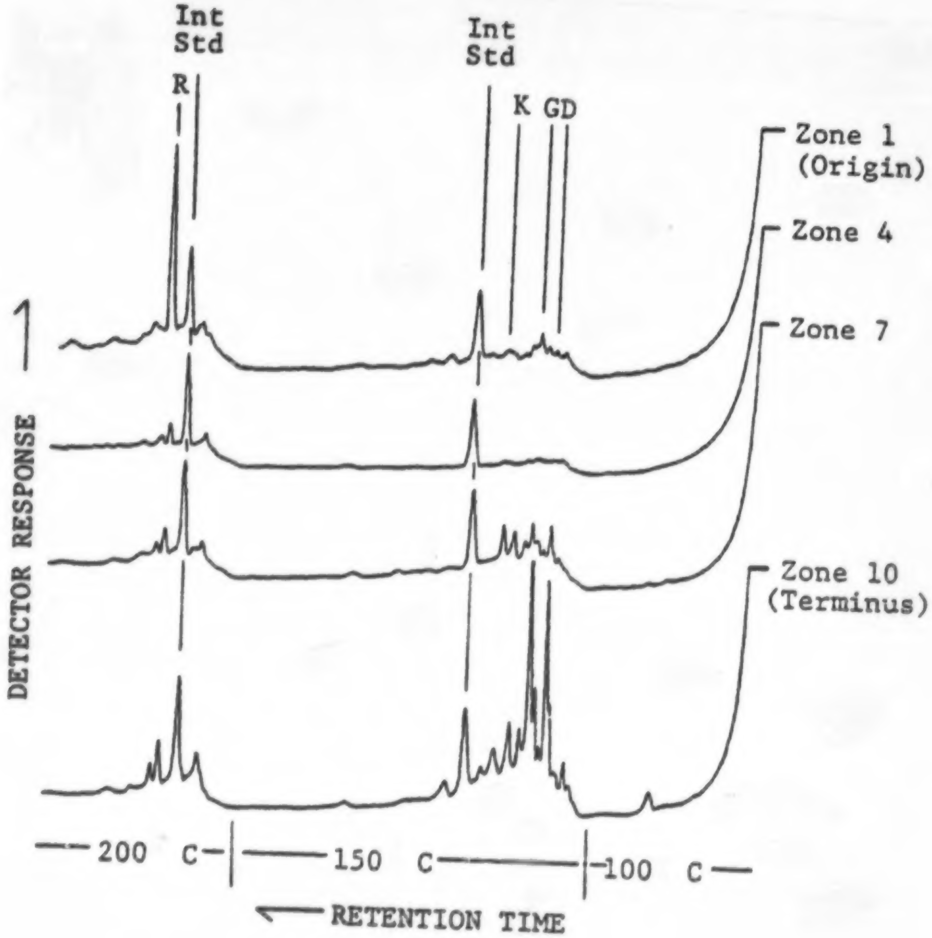


Figure 25. GLC visualization of soil TLC mobility distributions for the Norwood series.

High Molecular Weight Residues

After numerous injections of WSF samples into the gas chromatograph, a noticeable oily residue was visible in the injection port. Since the injector heat was set at 245 C, the residue probably consisted of high boiling materials

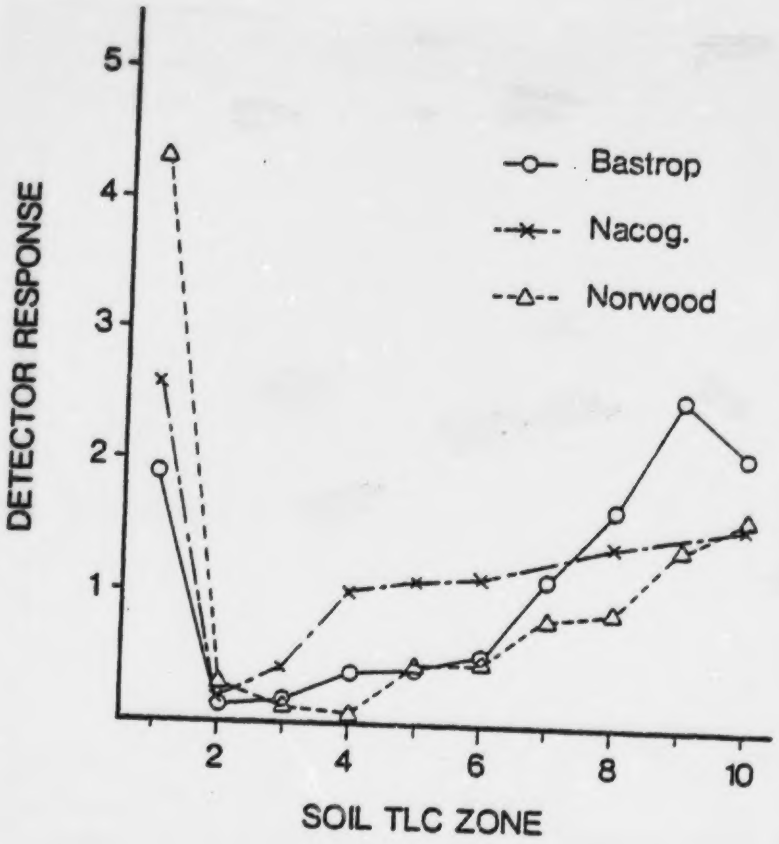


Figure 26. Mobility distribution on soil TLC of the portion of the WSF eluting at 150 C from GLC. Compounds move as a group, and the ordinate values are the summed peak heights averaged over three replicate soil TLC plates

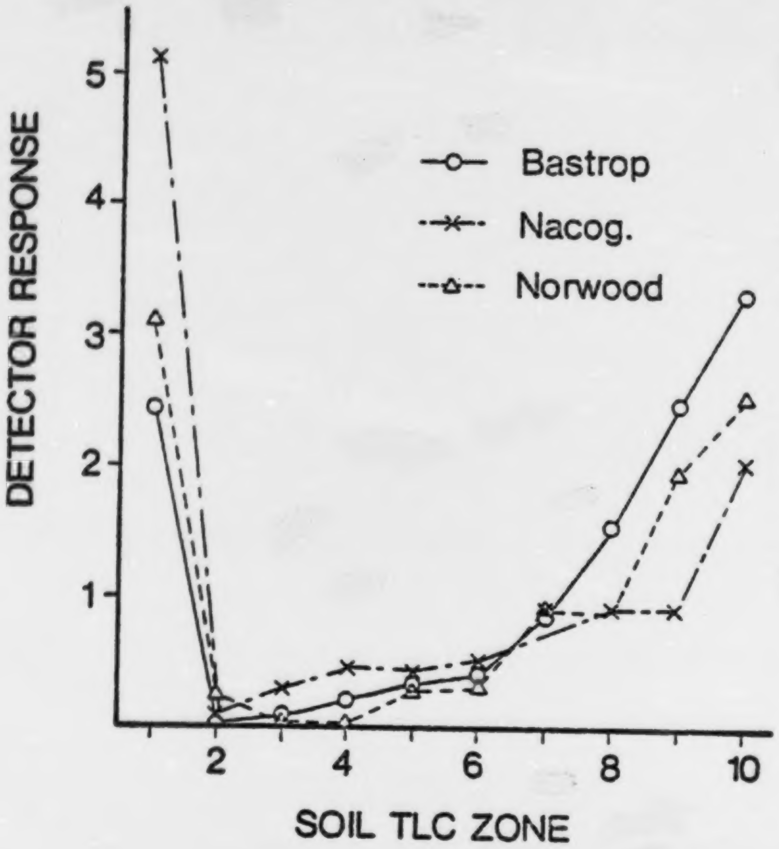


Figure 27. Mobility distribution of n-methyl-naphthalene (D) on soil TLC, averaging three replications for each of three soils.

such as polynuclear aromatics. However, they are not likely to be mobile in soil, as evidence by the soil TLC mobilities of the phtalates and other compounds eluting at 200 C.

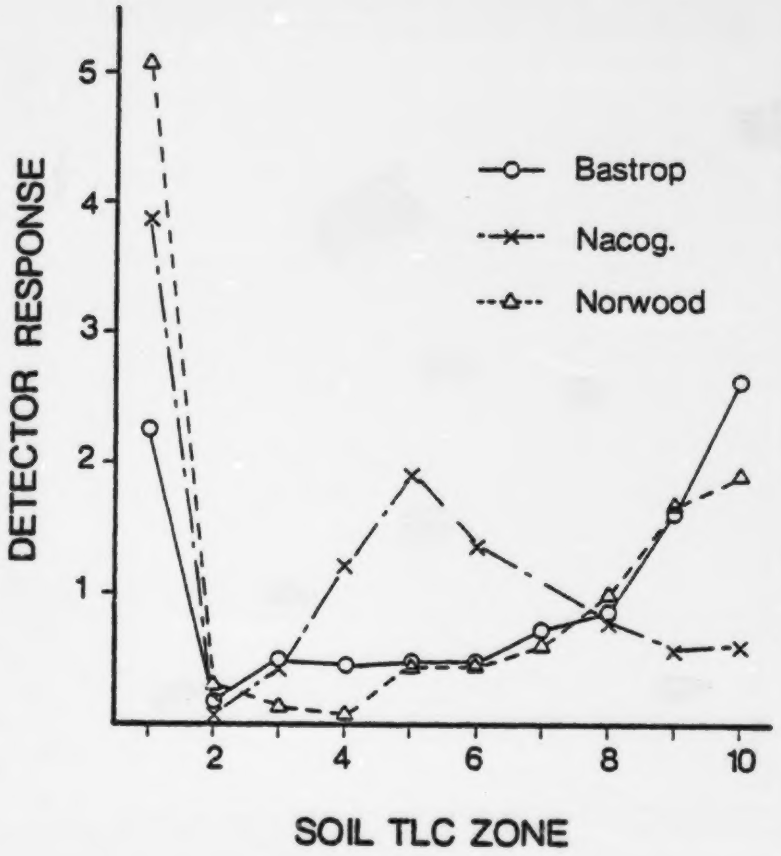


Figure 28. Mobility distribution of dimethyl-naphthalene and indan-1-one (G) on soil TLC, averaging three replications for each of three soils.

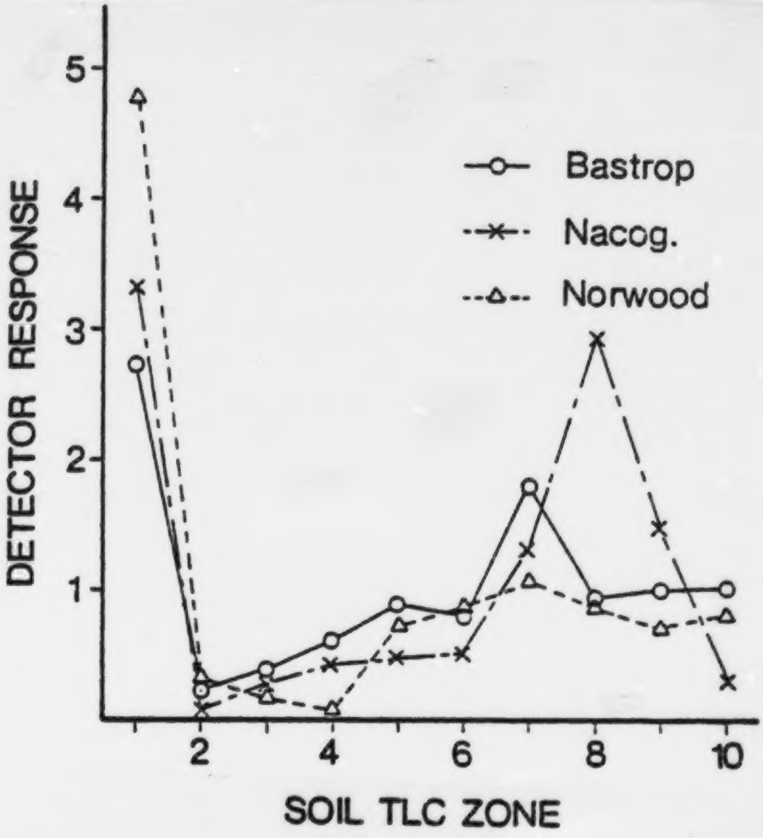


Figure 29. Mobility distribution of trimethyl-naphthalene and acenaphthene (K) on soil TLC, averaging three replications for each of three soils.

Determination by Soil Column

The leachate fractions from both of the sludge-treated Bastrop columns contained soluble organics as evidenced by GLC; however, a strong background of organics was also eluted from the control at matching retention times (Figure 31). Soluble soil organic matter effectively masked any of the waste compounds in the leachate so that no conclusive

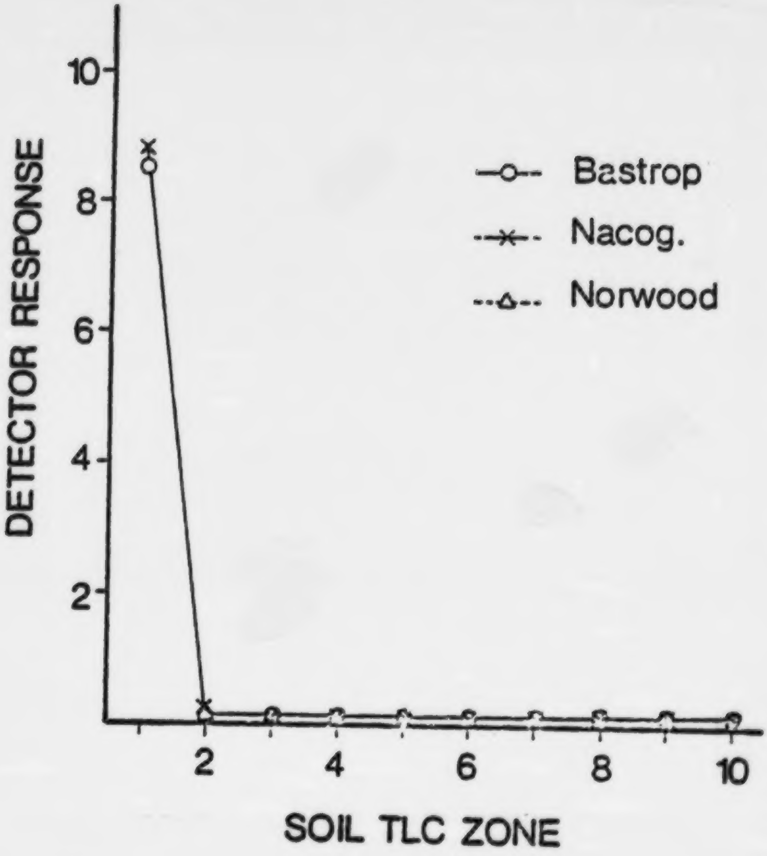


Figure 30. Mobility distribution of dibutyl phthalate (R) on soil TLC, averaging three replications for each of three soils.

evidence of mobility could be discerned from the columns. Nacogdoches and Norwood data paralleled the Bastrop results. Petroleum leaching studies by Raymond et al. (1976) and Dibble and Bartha (1979) agree with these results although they (questionably) concluded that no leachate contamination occurred. Development of a sample cleanup protocol would be beneficial for reliably monitoring low concentrations of organic contaminates in soil columns.

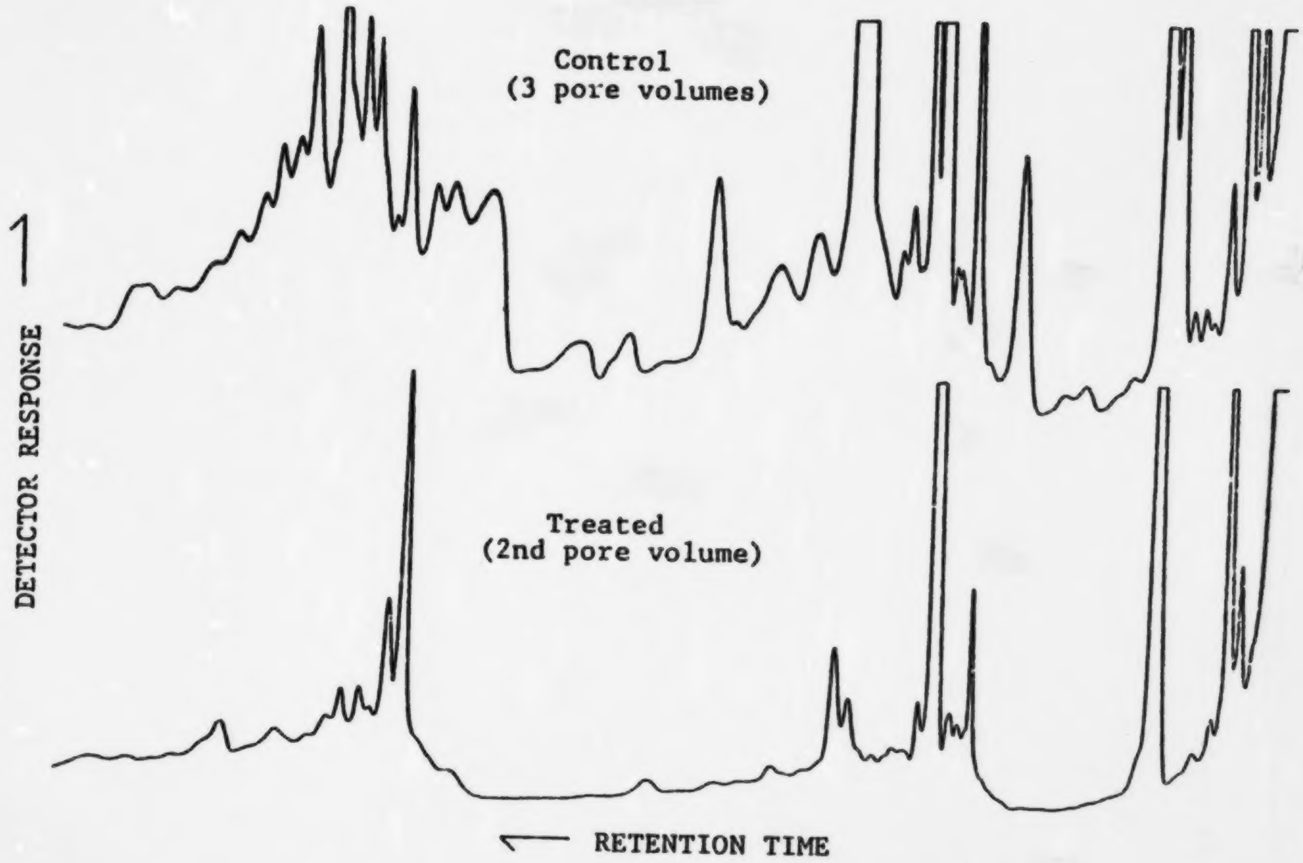


Figure 31. GLC scans of leachate extracts from the Bastrop series sludge-treated and control columns.

REVIEW OF INFORMATION ON IDENTIFIABLE COMPOUNDS

In order to set the characterization and mobility results into a frame work for assessing leachate hazards, specific information was obtained for the identified compounds in the WSF. Points of interest were the mechanisms that attenuate leaching and the toxicities of the compounds.

Degradation in Soil

As was previously discussed, aromatic compounds are less readily degradable by microbial activity, and knowledge of the metabolic pathways of ring cleavage and oxidation is limited. An important mechanism is co-oxidation, where the microbes begin by preferentially oxidizing the simpler available substrates, such as n-paraffins, and then adapt to the less suitable aromatics. The initial co-oxidative products of methylnaphthalene and dimethylnaphthalenes by *Nocardia* are methyl naphthoic acids which are not further degradable by this same species (Raymond *et al*., 1967). Naphthalene and some methylnaphthalenes were also degraded to single ring catechol and methyl catechols by *Pseudomonas* (VanDerLinden and Thijsse, 1965), where the ease of methylnaphthalene oxidation was a function of methyl group location. Additionally, *Flavobacterium* was found to degrade phenanthrene to hydroxy-naphthoic acid and subsequently to naphthoquinone. Under anaerobic conditions, such as in saturated soil or in the deeper soil horizons, ring fission has not been demonstrated since oxygenases from molecular oxygen are required for cleavage (VanDerLinden and Thijsse, 1965). Therefore, there is reason to expect longterm stability of any portion of the WSF reaching the subsoil or groundwater unless oxidized zones are present in the profile.

Acute and Chronic Toxicity

Much of the toxicity information on WSF components is from an industrial safety and health perspective which emphasizes acute symptoms resulting from large doses. However, potential leaching, runoff, or volatility losses from soil incorporation involve low levels as evidenced by the 24 ppm bulk concentration of the WSF equilibrated in water. Comparisons by Rossi *et al*. (1976) on the acute toxicity of water solubles from crude and refined petroleum found increased mortality in marine polychaetes exposed to the refined petroleum WSF. The results were attributed to differences in the levels of naphthalenes. Methyl- and dimethylnaphthalenes have been shown to be toxic to fish and crustaceans in concentrations as low as 0.1 ppm (Anderson et al., 1974). Extrapolation to a soil system or to terrestrial organisms would be difficult, but observed inhibition or phytotoxicity to soil microbial populations by oily waste application may be related in part to the presence of naphthalenes and other aromatics.

Of greater importance are the chronic effects to humans from lengthy low level exposure to the water soluble aromatics. Published listing of commonly recognized or suspected chemical carcinogens, such as by Fishbein et al. (1970), have not included the compounds found in the WSF, with the possible exception of phenanthrene. Three to five ring structures are generally considered to be more mutagenically active. However, benzene was historically considered as non-mutagenic but is currently implicated as a carcinogen (Thorpe, 1978). Therefore, the mono- and diaromatics which compose most of the WSF should be viewed with suspicion and their release into the environment should be minimized.

Other Considerations

Several additional factors can contribute to attenuation or enhancement of leaching. Studies by Lee et al. (1978) of the WSF from a number 2 fuel oil showed that aqueous solutions exposed to air for 12 hours lost over 80% of the naphthalenes by evaporation. By contrast, the phenols and indoles remained as near 50% of their original concentrations after 5 days. Additionally, Winters et al. (1976) have shown that naphthalenes are released to the water as a function of solubility such that a consistent low concentration with time would be expected in the percolating soil water. Cresol and phenols were found to be more soluble and can be expected to be moved as a pulse after waste application. Potentially significant concentrations of soluble waste degradation products may also accompany the WSF in the leachate. Subsoil characteristics, in particular the subsoil texture, CEC, structure, organic matter content, and permeability, can also be less accommodating to leaching. As predicted from hydrodynamic dispersion, the maximum concentrations from a spike of solute will decrease with depth (Boersma et al., 1972). Therefore, for a relatively deep water table, any readily soluble compounds which are present in small quantities should reach the groundwater only in low concentrations.

SECTION 7

FIELD MOBILITY STUDY ON WATER SOLUBLE CONSTITUENTS

INTRODUCTION

Land application of complex industrial wastes will result in the addition of numerous organic compounds to the receiving soil. Current literature indicates that while some organics degrade readily (Hubbell, et al., 1973) others may be quite resistant and persist in the soil for long periods of time (Alexander, 1981). The mobility of waste organics and their degradation products in soil are not well understood. Information must be developed on the fate and mobility of organic waste constituents in the soil so that land treatment units can be designed and managed to protect our groundwater resources.

This part of the study was conducted to evaluate the fate of two land-treated oily wastes under conditions as close as possible to those which would occur in the field.

MATERIALS AND METHODS

Field Procedures

This study involved the controlled application of two oil-water separator sludges to large undisturbed soil monoliths under field conditions. Soil samples were taken periodically to ascertain degradation and residual organics while leachate was collected and monitored for potential groundwater contaminants. To provide continuity, the same four soils and 2 sludges were used as in the phytotoxicity study. Physical properties of soils are given in Table 1 and waste characteristics are given in Table 2.

Lysimeters

A detailed description of the technique for installing the lysimeters used in this project is given by Brown et al. (1974). Briefly the technique is as follows: Casing 152.3 cm by 203.2 cm were fabricated from .63 cm thick steel plate. The casings were sandblasted, coated with epoxy base, heavy metal free paint (Shertar), and forced into the ground with pressure applied by two backhoes. The soil was dug away around the outside to relieve the pressure as the casings were pushed. Angle irons or plates were forced under the casings once they were in place. These were bolted temporarily to the angle iron used to reinforce the casings. A temporary top was also bolted in place. A crane was then used to lift the soil monolith enclosed in the metal box and roll it upside down. Porous ceramic suction cups were installed in the soil at the bottom of the profile. The tubes used to conduct the leachate to the surface were threaded through a 1.27 cm diameter PVC tube installed along the inside of one wall. A .63 cm thick steel bottom plate treated as described above was then welded to the lysimeter. The lysimeters were turned upright and installed in holes dug to receive them. The space around each lysimeter was filled with soil to assure that similar soil thermal gradients would develop in the enclosed monoliths.

Sample Collection

Collection of Leachate Water Samples: A schematic diagram of the water collection system is shown in Figure 32. Leachate from the bottom of each lysimeter was collected through 12 porous cups (Coors Type #70001-P-6-C). Each had a bubbling pressure of .5 bars, a conductivity of 1.2 $ml\ cm^{-2}\ min^{-1}\ bar^{-1}$ and a surface area of 38.8 cm^2.

Plexiglass caps were sealed to the open end of the cups with a water proof two part epoxy (Armstrong #34). Nylon tubes .159 cm in diameter were cemented into the plexiglass caps with another two part epoxy (Armstrong #6) which adheres well to nylon. The 12 tubes lead to a glass collection manifold on the soil surface. Nylon tubes of .32 cm diameter were used to convey the leachate to the graduated collection bottles in an air conditioned (12-20C) field hut. A continuous vacuum was maintained simultaneously on all the 20 collection bottles via a manifold. Each line coming in from the field was equipped with a stop cock. Each bottle was also equipped with an outflow tube which was similarly equipped with a stop cock. A continuous potential equivalent to -0.8 bar was maintained on the suction cups for the entire experiment. While the vacuum was on, the incoming stop cock was opened and the outflow was closed. Depending on the season, the 19 liter bottles had to be emptied every 1-7 days. First the volume of the accumulated water was recorded, then the vacuum was

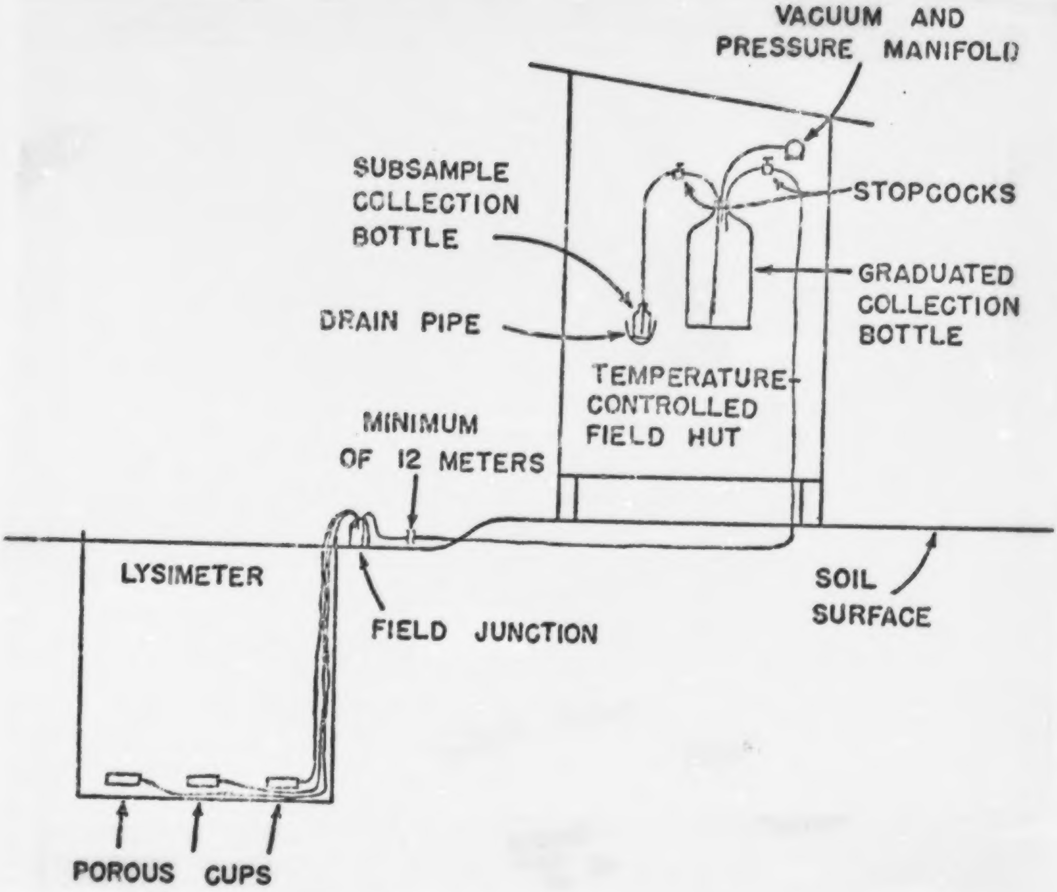

VACUUM AND PRESSURE MANIFOLD
SUBSAMPLE COLLECTION BOTTLE
STOPCOCKS
GRADUATED COLLECTION BOTTLE
DRAIN PIPE
TEMPERATURE-CONTROLLED FIELD HUT
MINIMUM OF 12 METERS
LYSIMETER
SOIL SURFACE
FIELD JUNCTION
POROUS CUPS

Figure 32. Schematic diagram of the sample collection system for the porous cups in the bottom of the lysimeters.

turned off. A valve was opened to bleed the vacuum from the system. During the bleeding, the incoming stop cocks were closed, and the glass sample bottles were positioned in the drain trough under the outflow line. Once the system was at atmospheric pressure, the stop cocks on the outflow line were opened, and the system was pressurized by means of a small pump. All of the accumulated water was forced out of the bottles into the sample containers. The excess water overflowed into the trough and drained away. As the collection bottles emptied, the outflow stop cocks were closed. After all bottles were emptied, the pressure pump was turned off, and the vacuum pump was turned on. The inflow lines were again opened. The entire process typically took about one hour, thus suction to the bottom of the lysimeters was only interrupted for short intervals.

The major difficulties that arose were caused by calcium carbonate accumulation, particularly in the lysimeters containing the Norwood soil. The calcium carbonate accumlation required periodic flushing of the manifold and the lines with a dilute solution of hydrochloric acid. This was done as needed immediately after the collection bottles were emptied; the flushing solution was discarded before the vacuum was reestablished. Occasionally tubes became blocked completely and sections needed to be replaced. In all cases, splicing was done by means of nylon tubes.

A geometric sampling scheme was employed in which samples of the leachate were collected from the following periods: 0-1, 1-3, 3-6, and 6-10 weeks after application. After 10 weeks, samples were taken at 4 week intervals (Table 23). When the sample container had to be emptied more frequently than called for on the above schedule, subsamples were collected and composited to represent the leachate for the sampling period. This entire sequence of leachate sampling was repeated after each waste application.

Leachate samples were collected in one or 2 l glass jars with teflon lined lids and transferred to the laboratory. All containers were cleaned with soap solution and sequentially rinsed with acetone, tap water and distilled water to remove all organics prior to sampling. All samples were refrigerated at 4 C after arrival at the laboratory.

Soil Sample Collection: Soil samples were collected at the following depths: 0-15, 15-30, 30-45, 45-90, and 90-150 cm. Soil samples were taken before application and at 1, 3, 6, and 12 months after application (Table 24). An additional set of soil samples were taken with a 2.22 diameter coring tool with a 25.4 cm cut away barrel. Soil sample locations were selected at random. The 0-15 cm sample usually did not provide enough sample for analysis so a second or third sample was taken in the plot and composited. All samples were stored in metal soil moisture cans in a freezer until analyzed. The use of plastics was avoided to prevent hydrocarbon contamination. Precautions were taken to avoid contamination of deep samples by surface material falling into the hole. These precautions included discarding the top of cores which may have been contaminated by soil falling in and wiping off the coring tool with a rag or washing it with clean water when this became necessary. Once the sampling was completed, a 149 cm long PVC tube was pushed into the hole to 1.27 cm below the soil surface to prevent short circuiting of rainwater. A tight fitting

TABLE 23. SCHEDULE FOR LEACHATE SAMPLE COMPOSITING

Sludge Application Date	Period	Sample No.	Weeks	Composite Over Dates
				1979
March 13, 1979	1	1	1	3-14 to 3-20
		2	2-3	3-21 to 4-3
		3	4-6	4-4 to 4-24
		4	7-10	4-25 to 5-22
		5	11-14	5-23 to 6-19
		6	15-18	6-20 to 7-17
		7	19-22	7-18 to 8-14
		8	23-26	8-15 to 9-11
		9	27-29	9-12 to 10-3
October 4, 1979	2	1	1	10-5 to 10-11
		2	2-3	10-12 to 10-25
		3	4-6	10-26 to 11-15
		4	7-10	11-16 to 12-13
		5	11-14	12-14 to 1-10-80
				1980
		6	15-18	1-11 to 2-7
		7	19-22	2-8 to 3-6
		8	23-26	3-7 to 4-3
		9	27-29	4-4 to 4-29
April 30, 1980	3	1	1	5-1 to 5-7
		2	2-3	5-8 to 5-21
		3	4-6	5-22 to 6-11
		4	7-10	6-12 to 7-9
		5	11-14	7-10 to 8-7

rubber stopper was put in the tube and the area was covered with a small amount of soil.

A complete set of soil samples was taken at each site when the lysimeters were filled. This included disturbed bulk samples and undisturbed core samples. Samples were collected to a depth of 1.5 m in all cases. These were taken to the laboratory and frozen until analyzed.

TABLE 24. SCHEDULE OF ACTIVITIES

Date		Activity
November 1, 1978	-	Start vacuum on lysimeters; begin collection of leachate.
November 8, 1978	-	Collect background soil samples (All lysimeters).
March 13, 1979	-	Apply petrochemical and refinery waste to two lysimeters of each soil type.
March 10, 1979	-	Installation of runoff system completed.
April 18, 1979	-	Soil samples (All lysimeters).
June 20, 1979	-	Soil samples (All lysimeters).
September 26, 1979	-	Soil samples (All lysimeters).
October 4, 1979	-	Reapply waste to one lysimeter of each soil type.
October 6, 1979	-	Add fertilizer and ryegrass seed to all plots.
December 31, 1979	-	Soil samples from lysimeters receiving second application only.
March 13, 1980	-	Ryegrass cover 50% for 16 of 20 lysimeters.
March 26, 1980	-	Soil samples (All lysimeters).
April 30, 1980	-	Third application both wastes to one lysimeter of each soil.
June 4, 1980	-	Till plots and sprig with bermudagrass.
October 24, 1980	-	Harvest lysimeters.
July 16, 1981	-	Soil samples (All lysimeters).

Grass Sampling: A stand of ryegrass was established in the lysimeters after the second waste application in October 1979. One week prior to the third application, all vegetation was cut and weighed. Subsamples were brought to the laboratory in plastic bags, the moisture content was measured, and the dry weight per unit area was calculated. No chemical analyses were made.

Soils

The same four soils used in the other sub-studies were used in this study. Detailed physical and chemical properties are given in Table 1. All monoliths were obtained from native areas which had not received waste applications of any kind.

Climatology

Rainfall was measured throughout the course of the experiment on a daily basis. A standard recording rainfall gauge was located within 5 m of the lysimeters. Rainfall throughout the experimental period is presented in Figure 33. Rainfall was rather similar to what is normal with more frequent and occasionally heavier rains in spring and fall months. Summer rains were generally less frequent and smaller. Total precipitation during 1979, 1980 and 1981 was 121.0, 66.3 and 107.2 cm, respectively.

Soil temperature at depths of 2.5 and 10 cm was measured using a Foxboro Model F100 MR temperature recorder. Charts were changed weekly and the data were analyzed and averaged to develop the plots shown in Figure 34.

Sludge Application

To assure uniform mixing of the sludge and soil, a 120 cm x 240 cm mixing board with 10 cm high sides was used. Twenty percent of the upper 0-15 cm of soil from a lysimeter was put on the board. The sludge was added and thoroughly mixed with the soil using hoes. Application rate was 5% by weight (1.1×10^5 kg/ha). The mixture was then evenly distributed over the entire surface of the lysimeter, tilled 10 cm deep by hand using shovels, and the surface was raked smooth. A schedule of which sludge was applied to which soil and the number of applications is given in Table 25.

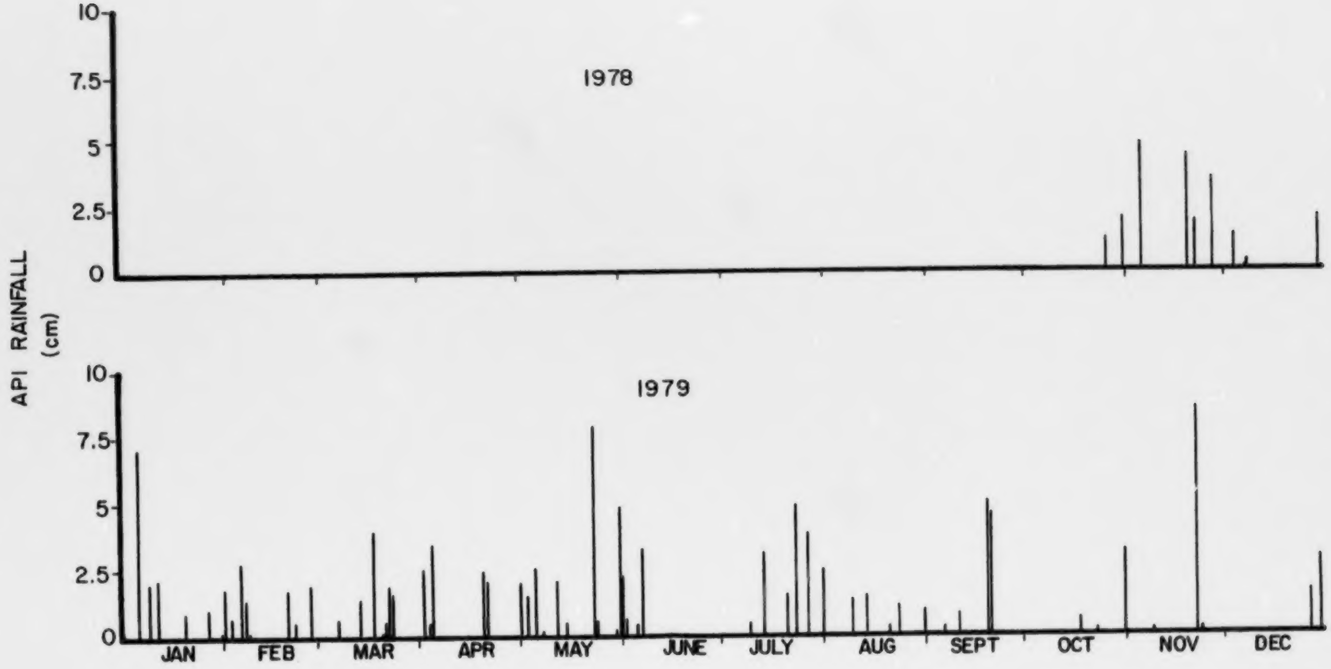


Figure 33. Rainfall at the field site during the experimental period.

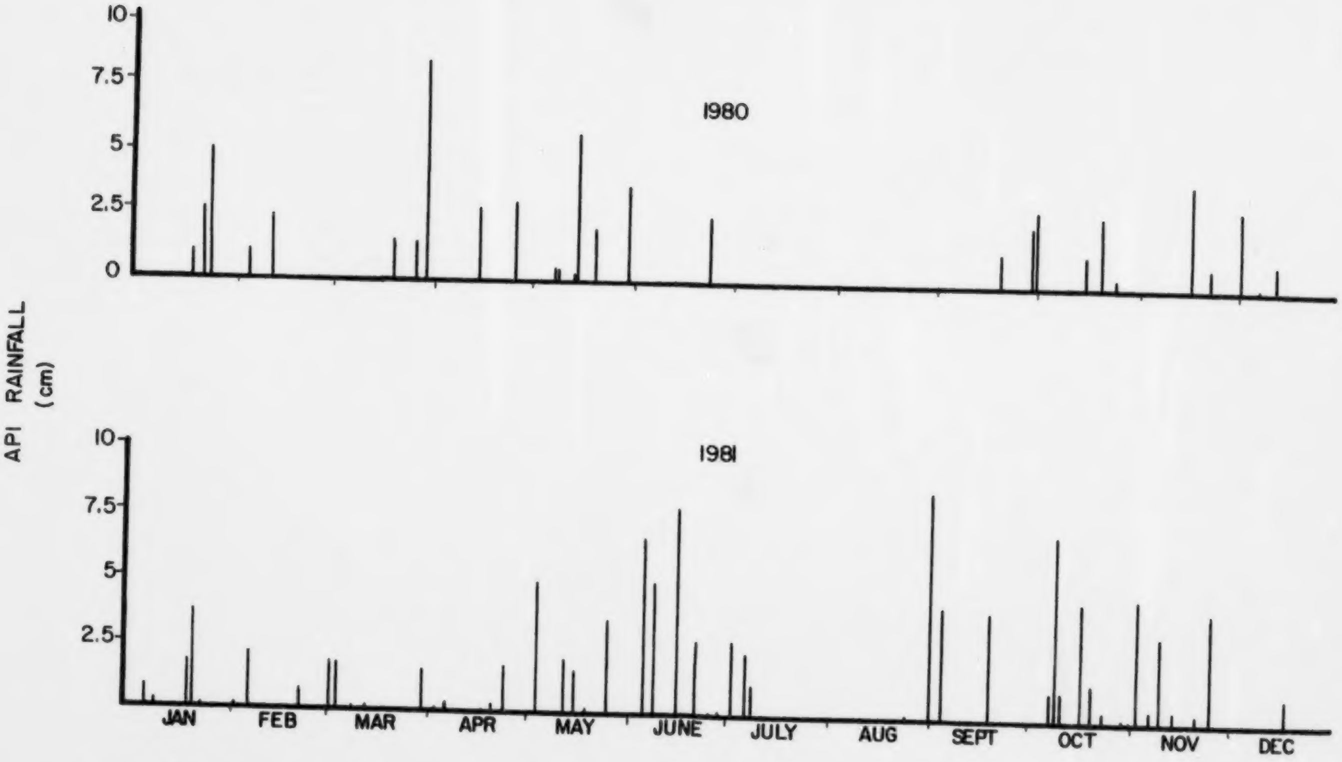


Figure 33 continued. Rainfall at the field site during the experimental period.

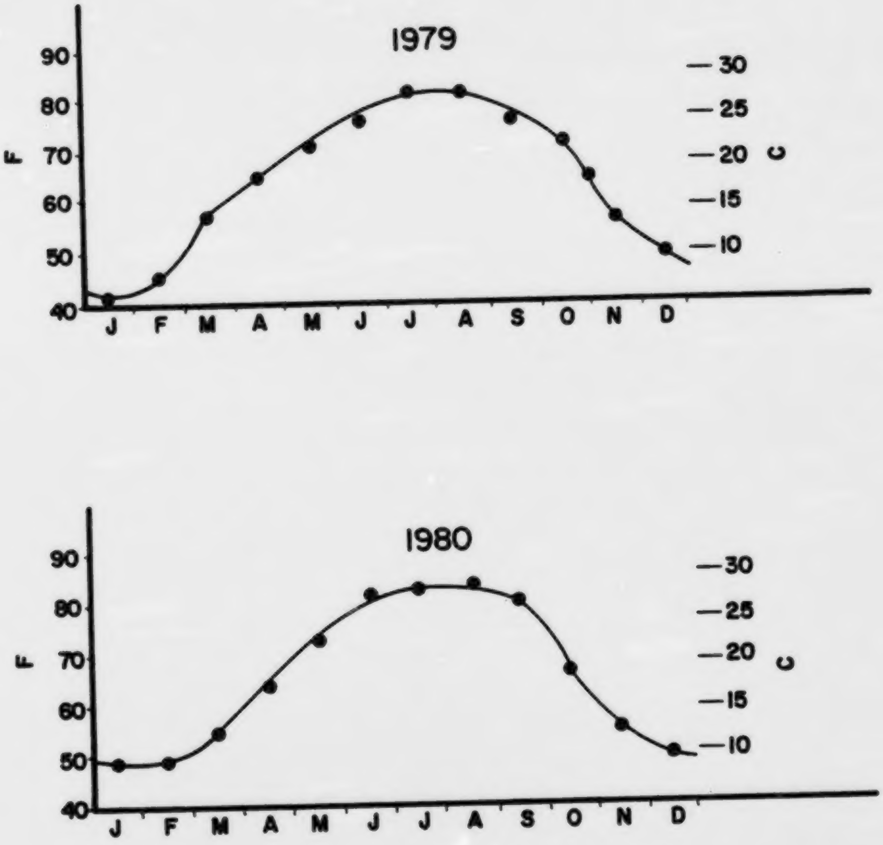


Figure 34. Average soil temperature in a lysimeter of Norwood soil at a depth of 6.4 cm during 1979 and 1980.

TABLE 25. SCHEDULE OF SLUDGE APPLICATIONS TO FIELD LYSIMETERS

Treatment	Soil	Lysimeter Number	Application Date 3-13-79	10-4-79	4-30-80
Refinery Sludge (R)	Nacogdoches	1	R	-	-
		2	R	R	R
	Lakeland	6	R	R	-
		7	R	-	R
	Norwood	11	R	-	-
		12	R	R	-
	Bastrop	16	R	R	-
		18	R	-	-
Petrochemical Sludge (P)	Nacogdoches	3	P	P	P
		4	P	-	-
	Lakeland	8	P	P	P
		9	P	-	-
	Norwood	13	P	P	P
		14	P	-	R*
	Bastrop	17	P	P	P
		19	P	-	R*
Control	Nacogdoches	5	-	-	-
	Lakeland	10	-	-	-
	Norwood	15	-	-	-
	Bastrop	20	-	-	-

* Lysimeter 14 and 19 received treatments of both refinery sludge and petrochemical sludge.

Waste Characterization

Water Content: Water content of the sludges was estimated by a vacuum distillation technique. Temperature was monitored at the level of the side arm delivery tube connected to a condenser and sample collector. The collector apparatus had a side arm and valves which provided a means for sample retrieval corresponding to discreet temperature intervals. Low molecular weight napthas and water co-distilled in a vapor phase which separated cleanly on condensation. Water was identified by its specific density and was reported as a weight percentage of the 100 g waste samples.

Residual Sediments: Residual sediment levels were estimated by thermal gravimetric analyses. Heat labile material was lost on ignition of the sample to 750 C in a muffle furnace. Samples weighed into crucibles were initially dried in a forced draft oven, prior to being heated at 250 C for 8 hours. The temperature was increased in 100 C increments to a temperature of 550 C with an 8 hour stay at each temperature step. Residues were cooled in a vacuum dessicator and weighed after 8 hours at 550 C. Residues were returned to the muffle furnace for a final curing at 750 C for 1 hour, allowed to cool and reweighed. No attempt was made to adjust residue weights for structural water loss from mineral fractions.

Organic Fraction Extraction: Three to 5 g samples of whole, homogenized sludge were weighed into a cellulose extraction thimble containing 25 g anhydrous Na_2SO_4 and mixed with a glass rod. The thimble and glass rod were placed in a 200 ml capacity Soxhlet extractor. Condensers and boiling flasks containing 200 ml of the appropriate solvent were assembled with the extractor and placed on the heater apparatus. Refrigerated coolant was circulated through the condensers. A 30 ml volume of solvent was introduced into the extractor from the top to facilitate flushing of the extractor chamber. Heat was applied to the boiling flask to initiate a 6 hour solvent extraction of the organic components; temperature was adjusted to give 6 flushings per hour. Waste samples were successively extracted with pentane, benzene, dichloromethane. The apparatus was disassembled between each solvent extraction to drain extractors and change boiling flasks.

Boiling flask contents were dried over a bed of anhydrous Na_2SO_4 into a larger flask and reduced to a 50 ml volume by vacuum distillation. A 5 ml aliquot was introduced into a weighed 10 ml beaker, and solvent evaporated to <0.5 ml with the aid of a gentle stream of dry nitrogen to the liquid surface. Solvent was finished evaporated from extracts by rolling the remaining liquid onto the beaker sides. Beakers were weighed immediately upon evaporation to determine extractant residue weight.

A separate 5 ml aliquot was reduced to <0.2 ml, followed by the addition of 2 ml hexane for loading onto a silica gel column employed to fractionate samples into organic class components.

Column Fractionation: Hydrocarbons were fractionated into saturates, aromatics, and higher condensed polynuclear aromatics, using the silica gel procedure developed by Warner, 1976, as modified by the EPA, Edison Laboratory.

Silica gel columns were prepared from bottom to top in the following manner: glass wool plug, 2 cm anhydrous Na_2SO_4, 10 g activated silica gel, and 2 cm anhydrous Na_2SO_4. Columns were rinsed with successive dichloromethane and petroleum ether washes. Samples were placed on the column and eluted with 25 ml petroleum ether to remove saturates from the sample matrix. A second 50 ml fraction containing aromatic hydrocarbons was eluted with 20% dichloromethane in petroleum ether. Carbazoles and some higher condensed polynuclear aromatics were eluted with 25 ml straight dichloromethane.

The various fractions were reduced in volume by vacuum distillation and taken just to dryness with a gentle stream of nitrogen. The first fraction containing the saturates was redissolved in hexane, and the other fractions were taken up on benzene.

Characteristic Gas Liquid Chromatographic (GLC) Profiles: GLC profile were developed using a temperature programmed Tracor Model 560 GC, equipped with dual flame ionization detectors. The GC was fitted with a 72 cm by 0.64 cm i.d. glass column packed with 3% OV-1 on 80-100 mesh chromosorb W. Injector temperature was maintained at 235 C. Column oven was programmed between 100 and 240 C at a rate of 3 C/min with an initial hold of 10 min and final hold of 40 min.

Quantification was accomplished by comparing detector response of unknowns to known amounts of reference materials. Detector response was measured electronically as an integrated peak area. A myriad of saturates, aromatics, and polynuclear aromatics were routinely employed in assessing detector response.

Due to the complexity of hydrocarbons in the waste streams, a certain fraction of the materials extracted could not be resolved into peaks but instead reflected a cone shaped elution pattern traced onto recorder paper. The integrators were set to work from a floating baseline, such that the area resolved as peaks did not include that under the cone. Complex hydrocarbon mixtures eluted as a cone were quantified as a carbon mass by comparison to planimeter areas of known hydrocarbon masses.

Hydrocarbons, for comparative purposes, were quantitated by peak area, by total peak area, and by total conical area differentiated above the carrier's solvent baseline.

Injection volumes, including a minimum 1 μl backwash, were always maintained as near equal to 4 μl as possible. Initial sample injections were generally 2.5 μl and a 1.5 μl backwash. Sample injection volumes deviating from 2.5 μl were materially balanced by the volume of backwash.

Mass Spectral Analyses: Gas chromatographic - mass spectral techniques were employed in the initial characterization of waste streams. A Hewlett-Packard Dodecapole 5890 A model with GC inlet was used in this effort. It has a mass resolution of one mass unit. A 18 m glass capillary column (2 mm i.d. coated with SP 2100) was used in the GC. The temperature of the GC oven was programmed to increase from 70 C to 260 C at a rate of 8 C/min.

A comparative study was conducted to correlate retention times for major peaks using a 6.4 mm by 1.8 m glass column packed with 3% OV-1 on 80/100 mesh chromosorb W. and a 2 mm by 18 m glass capillary column coated with SP 2100.

Organic Recovery from Soils

Petrochemical and refinery sludges were added to duplicate soil samples at a 10% (w/w) loading rate. Sludges were thoroughly mixed with an initial fraction of the soil mass, then mixed with the entire soil sample. Soils were oven dried at 105 C and finely ground prior to mixing in waste materials. The resultant mix was aged 48 hours and transferred to a glass blender vessel.

Wastes were extracted from the soil matrix by blending with 200 ml solvent for 15 minutes. Extractants were dried over anhydrous Na_2SO_4 and assayed gravimetrically for total hydrocarbons extracted.

Extraction efficiencies from soils were determined by comparing the quantities extracted by soxhlet from wastes in the absence of soil to those recovered by blending following soil incorporation.

Soil Sample Analysis

Organics were extracted from 10 to 20 g of soil by blending with 200 ml of 15% diethylether in CH_2Cl_2 for 15 minutes as described above. The extract was dried, brought to 50 ml volume and a 5 ml aliquot was fractionated as described earlier in the column fractionation section.

Water Sample Analysis

A 500 ml aliquot of each composite water sample was extracted three times with 50 ml volumes of dichloromethane by shaking for 1 min in a separatory funnel and removing the organic phase. The organic phase was then dried by passing it over anhydrous Na_2SO_4. It was then concentrated to 2 to 3 ml in a flash evaporator and a subsample was injected into the GLC. The detection limit was 34 μg/mg.

RESULTS AND DISCUSSION

Waste Characterization

A refinery sludge (RS) and petrochemical sludge (PS) were selected for in-depth laboratory characterization. Composition of the RS in percent of wet weight is presented in Table 26. Sequential Soxhlet extraction showed 9.9% of the waste was solvent extractable. Reversing the order of solvent had no affect on the total extractable value but drastically altered the distribution. Dichloromethane extracted 100% of the materials partitioned by solvents, with succeeding benzene and pentane fractions coming up clean. Greater than 85% of the RS wet mass was attributed to water and a non-extractable residue. An average of 37.8% of the wet weight components or 95% of the non-extractable and heat stable residue is attributed to structural water loss from the mineral fraction. The average total organic carbon (TOC) determined by wet oxidation and gravimetric assay of CO_2 absorbed was 7.3% on a wet weight basis (Table 26). This value compares favorably to the total extracted value considering hydrocarbons contain other elements than just carbon.

Composition of the PS in percent of wet weight is presented in Table 27. The total solvent extractable component was 62% of the whole sludge. Water comprised 11.9% of the sludge, and a residue comprised the remaining 25.1%. An average of 99% of the total wet mass was conserved within the component distribution given. However, the average residue stable to 750 C was diminished to only

TABLE 26. COMPOSITION OF REFINERY SLUDGE (RS) IN PERCENT OF WET WEIGHT

Parameter	Percent of* Bulk Sludge (w/w)
Water	45.7
Soxhlet Extractable (Total)	9.93
Pentane fraction	7.17
Benzene fraction	2.20
Dichloromethane fraction	0.56
Residue	
Air dry	40.6
Stable to 750 C	37.8
Sulfur	0.88
Nitrogen	0.09
Carbon (wet combustion)	7.3

* Average of multiple determinations.

8.2% of the whole waste mass, or less than 33% of the non-extractable residue level. The differential in weight loss cannot be accounted for as structural H_2O due to the magnitude. Carbonaceous minerals may be ruled out since the wet oxidation and gravimetric analysis of CO_2 evolved gave an average TOC of 44.2%. This suggests that a significant fraction of the hydrocarbons in the PS are not extracted by Soxhlet technique but are heat labile at 750 C. No attempt was made to further characterize this fraction due to lack of methodology and the assumption of a low reactivity in soils.

Soxhlet extracts of sludge were fractionated on silica gel to determine the relative distribution of hydrocarbons eluted as saturates and aromatics(Table 28). Residue recovered in Fraction 1 was assayed gravimetrically to

TABLE 27. COMPOSITION OF PETROCHEMICAL SLUDGE (PS) IN PERCENT OF WET WEIGHT

Parameter	Percent of* Bulk Sludge (w/w)
Water	11.9
Soxhlet Extractable (Total)	62.0
Pentane fraction	39.4
Benzene fraction	21.9
Dichloromethane fraction	0.7
Residue	
Air dry	25.1
Stable to 750 C	8.2
Sulfur	0.39
Nitrogen	0.11
Carbon	42.4

* Average of multiple determinations.

determine saturate levels. A composite of Fractions 2, 3 and 4 was employed to estimate the aromatic content. Residue recovered in the saturate fraction was divided by the total residue for both saturates and aromatics to estimate the relative percentage of the former. A similar computational exercise was performed to estimate aromatic weight percentages. The resultant distribution of hydrocarbons show the RS to contain almost a 2 to 1 saturate to aromatic hydrocarbon ratio. PS was distributed as 99% aromatics and 1% saturates.

Gas Liquid Chromatographic Characterization

Detector Response: Gas liquid chromatographic (GLC) analysis in conjunction with column fractionation on silica gel was used to develop characteristic chromatograms of

TABLE 28. DISTRIBUTION OF HYDROCARBONS AS DETERMINED GRAVIMETRICALLY FOLLOWING A FRACTIONATION OF EXTRACTS ON SILICA GEL

	Percent Hydrocarbons	
Waste	Saturates	Aromatic
Refinery	64	36
Petrochemical	1	99

sludge hydrocarbons.

A complex mixture of standards was injected to evaluate GC column conditions and detector response over daily, weekly, and monthly time intervals. Detector response, reported in integration units per mole of carbon for the various hydrocarbons injected, averaged over time is presented in Table 29. Response in integration units per mole of carbon averaged over compounds and the standard deviation about the mean are also presented in Table 29. The column in line with Detector 2 did not resolve n-docosane and phenyl carbazole into separate peaks. Thus the value reported was computed relative to the total carbon between the two. These data suggested that the detector response to hydrocarbons was relatively constant for a given instrument setting, when normalized on a per mole carbon basis. This standard deviation reflects variability over a 4 month time interval and shows that the innate differences between compounds are manageable in quantitating materials relative to carbon. A detector response of 10,000 integration units corresponds to 100 ng C ± 18 ng C for Detector 1 and 80 ng C ± 10 ng for Detector 2. The evaluation of detector response relative to moles of known material reflected the highly variable constituency of the compounds.

This discussion is not intended to imply the applicability of long-term averages for quantification purposes - certainly daily standard injections are paramount for quality assurance - but is presented to describe the utility of the technique employed when dealing with complex unknowns. Internal standards added to unknown mixtures may not necessarily reflect the class of compounds chromatographed, which parallels the inherent errors in quantitation observed when detector response was evaluated on a per mole compound basis.

Column Chromatographic Fractionation: The standard mixture (Table 29) was fractionated on silica gel (Figure 35). The utility of this procedure to potentially reduce the complexity of chromatograms for evaluation of various classes of compounds in a sludge is reflected in the separation of saturates, aromatics, and carbazoles. Saturates were clearly separated from the standard mixture. Fractions 2 and 3 were combined due to an inconsistent separation of di- and tri- aromatic compounds from polynuclear aromatic materials, as reported in the procedural paper of Warner, 1976. Fraction 4 contained the two carbazoles added in the standard mixture, although significant quantities of both were eluted in combined Fractions 2 and 3.

TABLE 29. FLAME IONIZATION DETECTION RESPONSE TO HYDROCARBONS

Peak No.	Compound	Detector Response*	
		Detector No.1	Detector No. 2
1	1,2-diphenylethane	1.26×10^{12}	1.59×10^{12}
2	Xanthene	0.89×10^{12}	0.92×10^{12}
3	Dibenzothiophene	1.25×10^{12}	1.54×10^{12}
4	Anthnacene	1.16×10^{12}	1.37×10^{12}
5	n-Ethyl Carbazole	1.33×10^{12}	1.70×10^{12}
6	p-Terphenyl	1.24×10^{12}	1.50×10^{12}
7	Fluoranthene	1.32×10^{12}	1.62×10^{12}
8	n-docosane	1.16×10^{12}	1.60×10^{12}
9	n-Phenyl Carbozole	1.37×10^{12}	
10	Hexacosane	1.15×10^{12}	1.61×10^{12}
11	Cholestane	0.99×10^{12}	1.53×10^{12}
	Avg.	1.19×10^{12}	1.50×10^{12}
	Std. dev ($\sigma\pm$)	0.18×10^{12}	0.18×10^{12}
	No observations	550	500

*Detector response reported as integration units per mole of carbon.

Silica gel fractionation of a Soxhlet extraction of RS with dichloromethane is given in Figure 36. The results of the total hydrocarbons quantitated by GLC as carbon for the whole extract and column fractions are given in Table 30. Peaks were quantitated by comparing the detector response of standards to the total integrated peak areas. The cone represents that envelope of hydrocarbons eluting from the GC

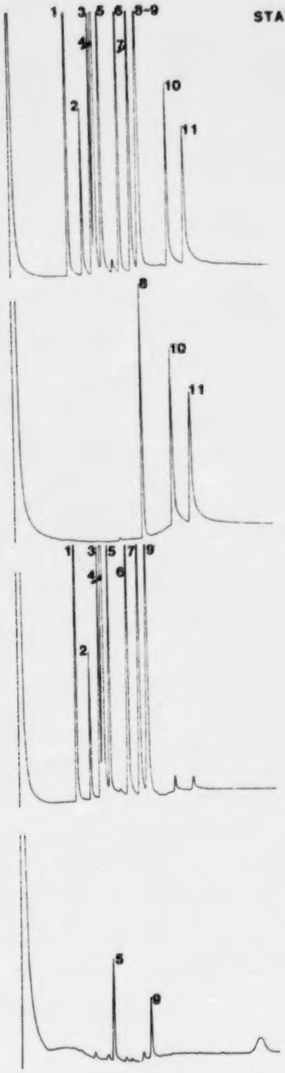


Figure 35. Chromatrographs of Standard Compounds.

TABLE 30. TOTAL HYDROCARBON MEASURED BY GLC FOR THE WHOLE EXTRACT AND THE FOUR FRACTIONS OF THE REFINERY SLUDGE

Refinery Sludge	Detector Response to Carbon Peaks	 Cone	 Total	Recovery*
	μg/g			%
Whole Extract	52,889	10,239	63,128	
Fraction 1	21,350	6,604	27,954	44.3
Fraction 2 & 3	10,671	4,579	15,250	24.2
Fraction 4	3,182	3,063	6,245	9.8

*Percent of whole extract recovered from column.

column but not resolved as peaks. Cone areas were established by planimeter and compared to known carbon areas established with the planimeter. Total carbon quantitated by GC analysis of the whole extract represents 86% of the total organic carbon (73,000 μg/g) determined by the wet combustion technique. Approximately 44% of the whole sludge extract was recovered from silica gel in the Fraction 1 eluant. Seventy six percent of Fraction 1 was resolved as an integrated peak area. Combined Fractions 2 and 3, theoretically representative of mono-, di-, tri- and polynuclear aromatics, comprised 24% of the whole extract eluted from silica gel. Carbazoles and higher condensed polynuclear aromatics recovered from silica gel in the Fraction 4 eluant comprised approximately 10% of the whole extract. About 78% of the whole extract was recovered from silica gel. A lower percentage of the aromatic hydrocarbons was resolved as peaks. Approximately 70% of total hydrocarbons assayed for combined Fractions 2 and 3 were resolved as peaks. Less than 51% of the total hydrocarbons recovered in Fraction 4 was resolved as an integrated peak area. The cone area is not readily apparent in the chromatographs shown in Figure 36 due to the dilution of fractions employed in presenting the more diagnostic peak patterns. However, the cone shape or envelop pattern indicative of a complex matrix has diagnostic features characteristic of the source.

Silica gel fraction of the PS Soxhlet extracted with dichloromethane is graphically depicted in Figure 37. Chromatograms show a definite distribution towards an aromatic character. GLC profiles of saturates (Fraction 1)

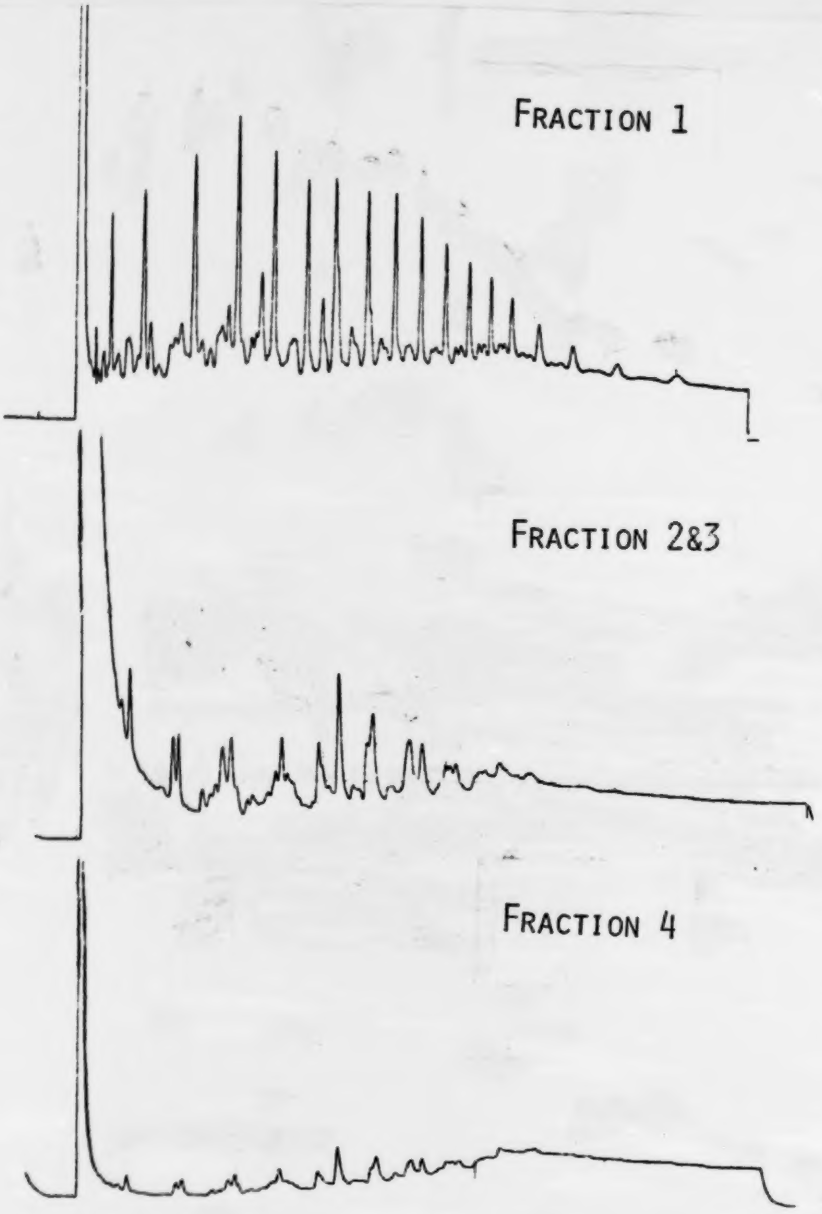


Figure 36. Soxhlet extracted refinery sludge.

and higher condensed polynuclear aromatics (Fraction 4) were developed for eluants at the same material dilution. Combined Fractions 2 and 3 were diluted 1 to 10 with benzene to resolve the peaks on chart paper. Hydrocarbons quantitated by GLC for the various fractions resolved as peak and conical areas are summarized in Table 31. Total carbon recovered in whole extract, as detected by GLC analysis, was 28.3% on a sludge wet weight basis. The extracted total reflected 67% of the total organic carbon assayed (42.4% on a wet weight basis) by the wet combustion technique. Percent saturates, aromatics and higher condensed polynuclear aromatics recovered from the silica gel fractionation of the whole extract were 0.9, 84, and 2.6, respectively. Carbon recovered as an area under the cone increased in direct correspondence to fraction number.

TABLE 31. TOTAL HYDROCARBON MEASURED BY GLC FOR THE WHOLE EXTRACT AND THE FOUR FRACTIONS OF THE PETROCHEMICAL SLUDGE

Petrochemical Sludge	Detector Response to Carbon			Recovery*
	Peaks	Cones	Total	
	µg/g			%
Whole extract	192,739	90,440	283,119	
Fraction 1	2,293	287	2,580	0.9
Fractions 2 & 3	163,476	74,360	237,836	84.0
Fraction 4	216	7,200	7,416	2.6

*Percent of whole extract recovered from column.

Molecular Weight and Carbon Number: A linear regression model was used to describe the relationships between retention time (RT) and molecular weight (MW). RT corresponding to peak sensitivity for compounds used in the standard mixture and others including napthalene, biphenyl, methyl heptadecanoate, and 9,9'-bifluorene were found to increase linearly with increased MW (Figure 38). Values (RT) averaged for multiple injections of known compounds of varying MW gave a regression coefficient (r^2) of 0.84. These data suggest that hydrocarbons with less than .76 g/mole would be eluted with the solvent front at the same column and instrument conditions employed for standards. A 20 minute increase in retention time roughly corresponds to

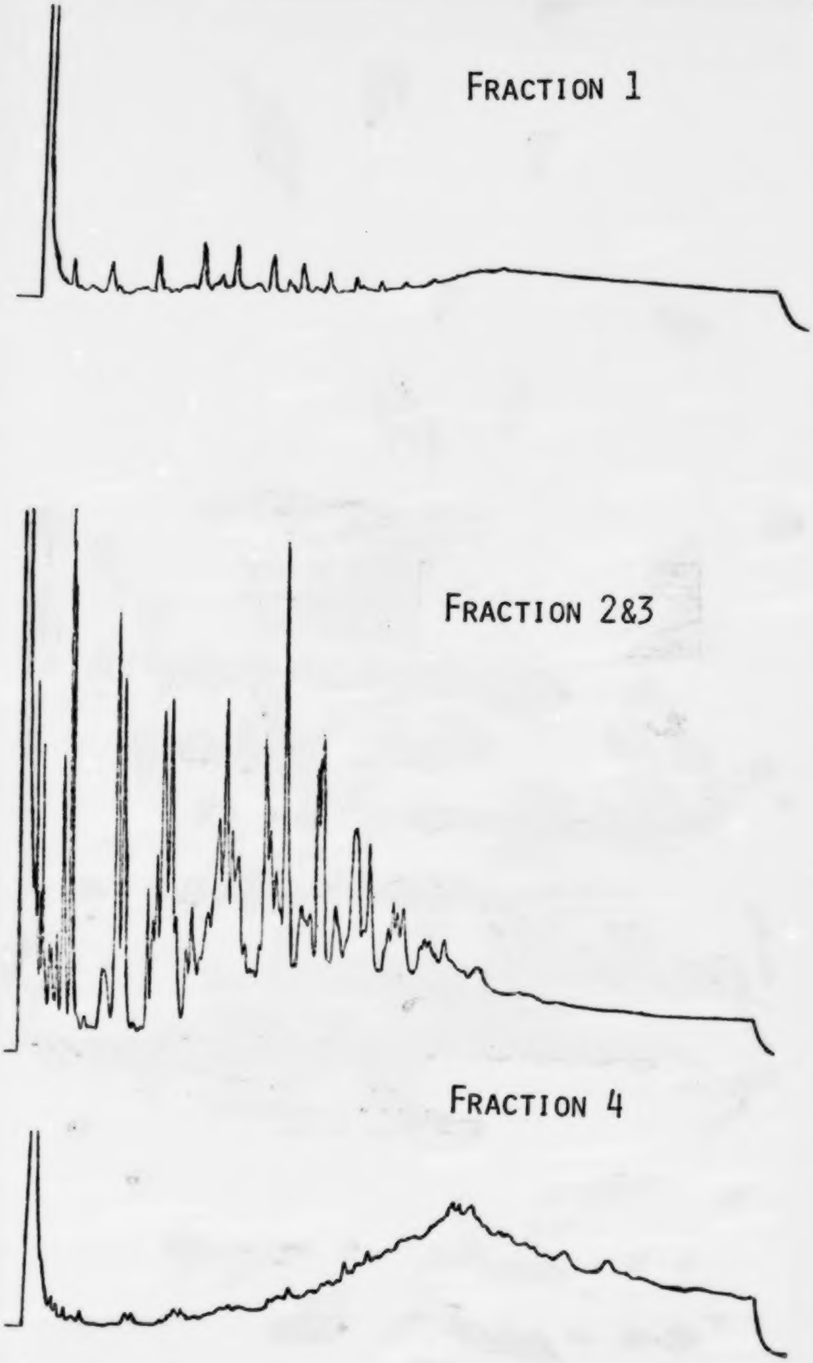


Figure 37. Soxhlet extracted petrochemical sludge.

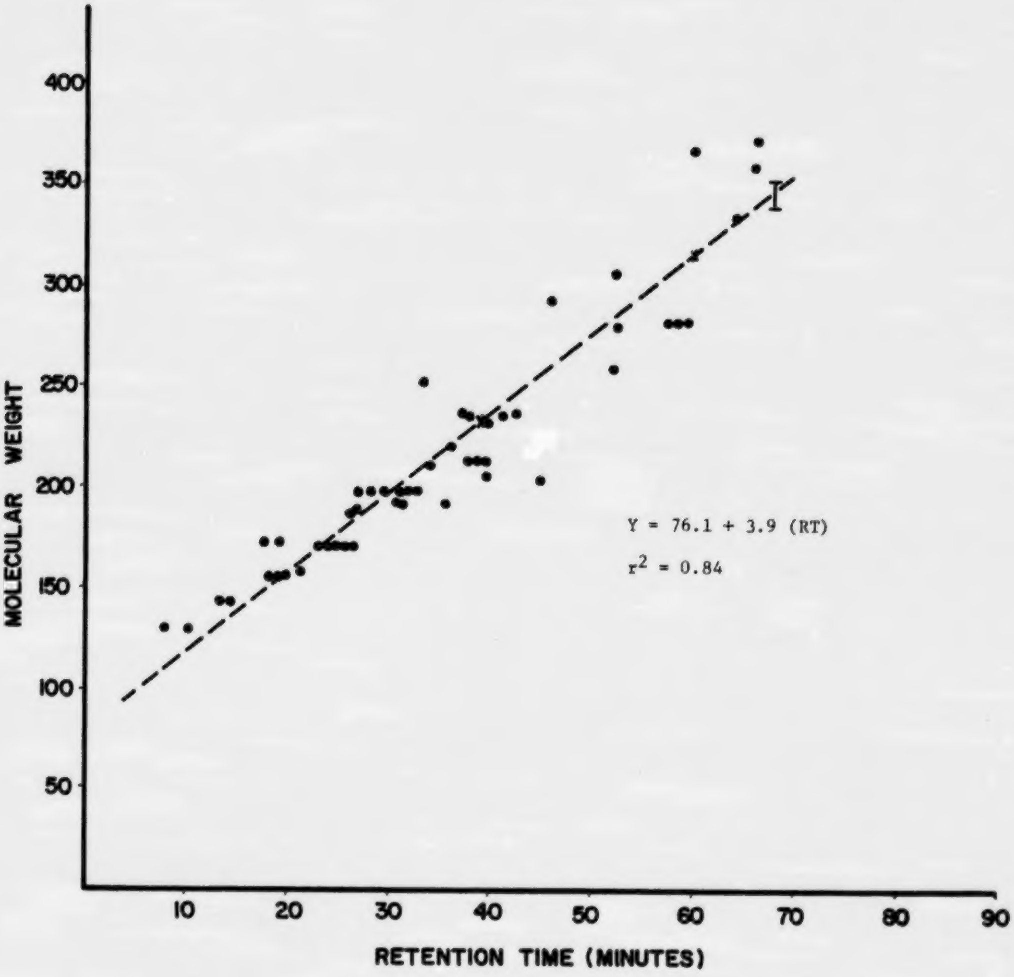


Figure 38. Relationship between retention time and molecular weight of known compounds.

5 carbons units added in chain configuration for saturates, or a benzene ring added for aromatics.

Similar results are reflected in the linear regression of RT and carbon number (Figure 39). Again the fit of the model ($r^2 = 0.83$) suggests that carbon number increases in linear proportion to the RT as described by the equation shown in Figure 39.

Chart speed was always maintained at 0.25 cm/min and was checked periodically by linear calibration to a stop watch. Molecular weight and carbon number (CN) were calculated for 18 peaks chromatographed in the saturate fraction of the RS (Figure 36) using corresponding RT's (Table 32). By dividing the MW obtained by the carbon number, one may predict a MW for carbon in excess of 12. Saturates are classed by the degree of hydrogen saturation. By dividing the known MW of carbon by that obtained in the exercise above and multipling by 100, the relative percent of carbon for the compound eluted is derived. The average of 88% carbon for the saturate fraction is certainly within reason.

TABLE 32. CALCULATED MOLECULAR WEIGHTS AND CARBON NUMBERS FOR SATURATE FRACTIONS OF RS

Peak No.	Retention Time (min)	Hydrocarbon Property Molecular Weight (g/mole)	Hydrocarbon Property Carbon Number
1	5.2	96.4	7.6
2	9.6	113.5	8.9
3	16.0	138.5	10.6
4	21.6	160.3	12.1
5	26.4	179.1	13.4
6	30.8	196.2	14.6
7	34.4	210.3	15.5
8	38.4	225.9	16.7
9	42.0	239.9	17.6
10	45.6	253.9	18.6
11	48.8	266.4	19.5
12	51.6	277.3	20.2
13	54.4	288.3	21.0
14	57.2	299.2	21.7
15	60.4	311.7	22.6
16	64.8	328.8	23.8
17	70.8	352.2	25.4
18	78.4	381.9	27.5

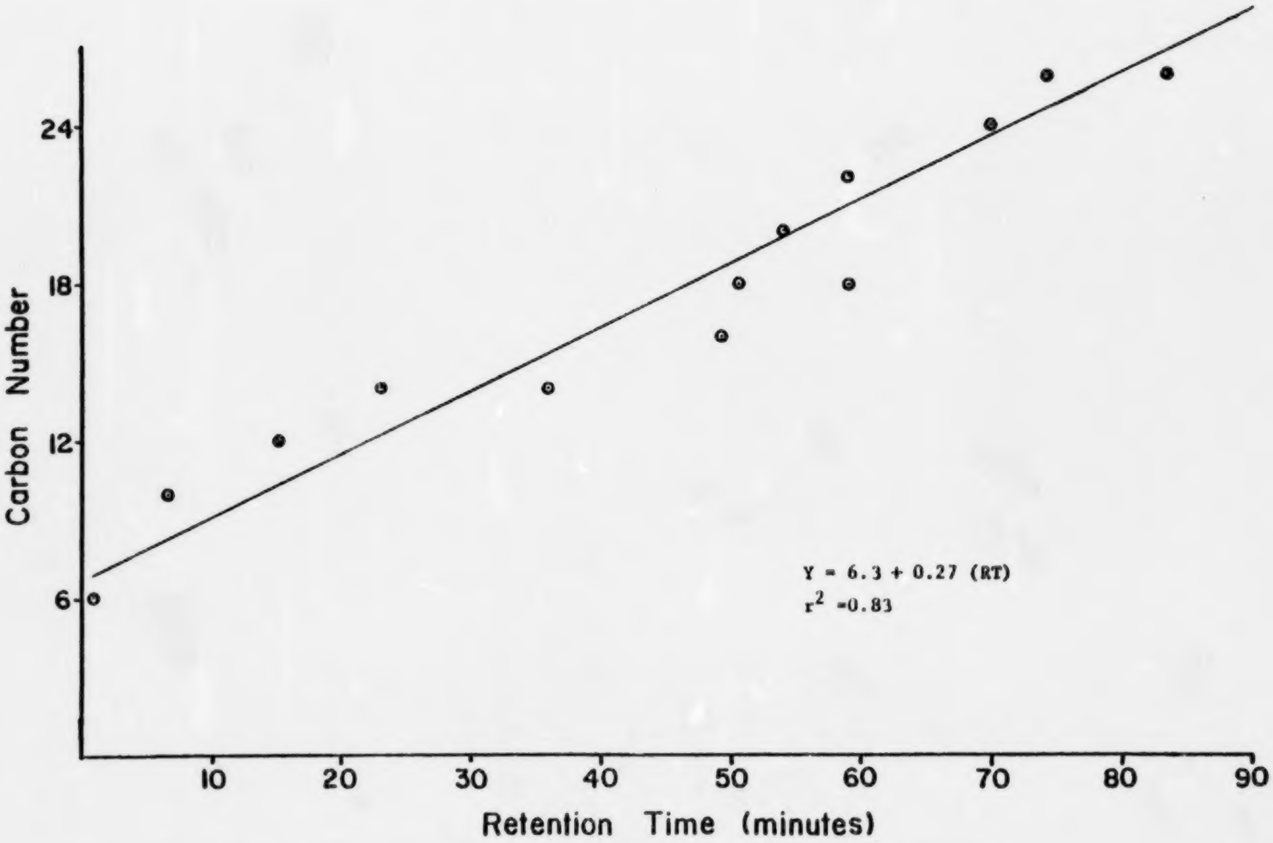


Figure 39. Relationship Between Retention Time and Carbon Number of Known Compounds.

As noted earlier, aromatics eluted in Fractions 2 and 3 comprised the bulk of hydrocarbons extracted and chromatographed (Table 32). Molecular weights and carbon numbers calculated from corresponding retention times of numbered peaks (Figure 37), using the models developed for the standard mixture, are given in Table 33. Predicted molecular weights and carbon numbers compare favorably to those actually determined by mass spectral analysis (Table 34) using interpretation techniques, in combination with Cornell University's computer program for mass spectra indentification. A possible structure type is suggested from spectra developed for numbered peaks. The mass spectrum was made for both the rise and fall of the peak elution pattern.

TABLE 33. CALCULATED MOLECULAR WEIGHTS AND CARBON NUMBERS FOR COMBINED FRACTIONS 2 AND 3 OF PS

Peak No.	Retention Time (min)	Hydrocarbon Property	
		Molecular Weight (g/mole)	Carbon Number
1	12.9	126.5	9.8
2	13.8	129.9	10.0
3	20.1	154.5	11.8
4	21.0	157.8	12.0
5	27.2	181.9	13.6
6	28.0	185.1	13.8
7	28.8	188.3	14.1
8	29.6	191.3	14.3
9	32.1	201.3	15.0
10	32.7	203.7	15.1
11	33.6	206.9	15.4
12	34.7	211.4	15.7
13	39.1	228.7	16.9
14	39.9	231.5	17.1
15	41.9	239.3	17.6
16	44.2	248.5	18.2
17	44.2	248.5	18.2
18	45.8	254.6	18.7
19	49.0	267.2	19.5
20	50.5	272.9	19.9
21	55.9	294.0	21.4

A linear regression model was used to statistically compare molecular weight and carbon number calculated from

TABLE 34. SUMMARY OF MASS SPECTRAL ANALYSIS OF COMBINED FRACTIONS 2 AND 3 FOR PS

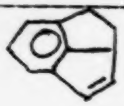
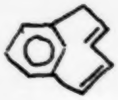
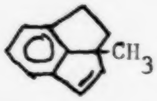
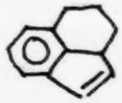
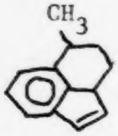
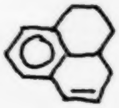
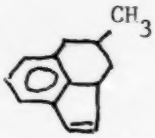
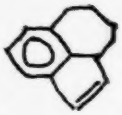
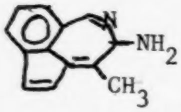
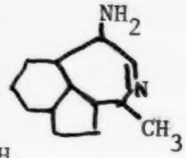
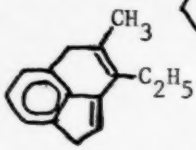
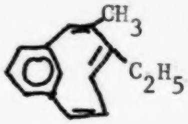
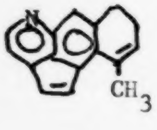
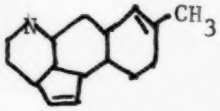
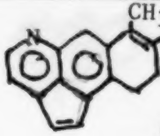
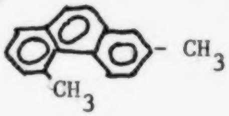
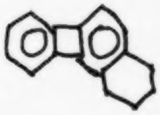
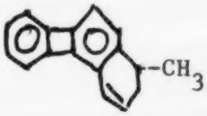
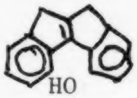
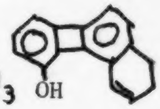
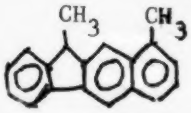
Peak No.	Retention Time (min)	Molecular Weight (g/mole)	Formula	Type of Structure
1	12.9	140	$C_{11}H_{10}$	
2	13.8	140	$C_{11}H_{10}$	
3	20.1	156	$C_{12}H_{12}$	
4	21.0	156	$C_{12}H_{12}$	
5	27.2	170	$C_{13}H_{14}$	
6	28.8	170	$C_{13}H_{14}$	
7	28.8	170	$C_{13}H_{14}$	
8	29.6	170	$C_{13}H_{14}$	
9	32.1	196	$C_{13}N_2H_{12}$	
10	32.7	196	$C_{13}N_2H_{12}$	
11	33.6	196	$C_{15}H_{16}$	
12	34.7	196	$C_{15}H_{16}$	
13	39.1	219	$C_{16}H_{13}N$	
14	39.9	219	$C_{16}H_{13}N$	

TABLE 34. CONTINUED.

Peak No.	Retention Time (min)	Molecular Weight (g/mole)	Formula	Type of Structure
15	41.9	233	$C_{17}H_{15}N$	
16	44.2	206	$C_{16}H_{14}$	
17	44.2	206	$C_{16}H_{14}$	
18	45.8	218	$C_{17}H_{14}$	
19	49.0	220	$C_{16}H_{12}O$	
20	50.5	220	$C_{16}H_{12}O$	
21	55.9	244	$C_{19}H_{16}$	

GLC retention times with those determined by GC mass spectral analyses. Ideally, a slope of one is obtained when the calculated and actual values are equal. The observed correspondence for molecular weights and carbon numbers are shown in Figures 40 and 41, respectively. The correlation coefficients (r^2) were high, demonstrating the utility of estimating molecular weights and carbon number from retention time. Deviation of the observed values from the ideal suggested that the computational models underestimated molecular weight and carbon numbers to 165 g/mole and 13, respectively. Calculated values overestimated those actually observed for compounds with GLC retention times exceeding 24 minutes. Aromatic standards used to develop the computational model compare in ring numbers but generally were more condensed and aromatic in character. The more open arrangement of PS aromatics tended to give longer retention times indicative of higher molecular weight materials than present.

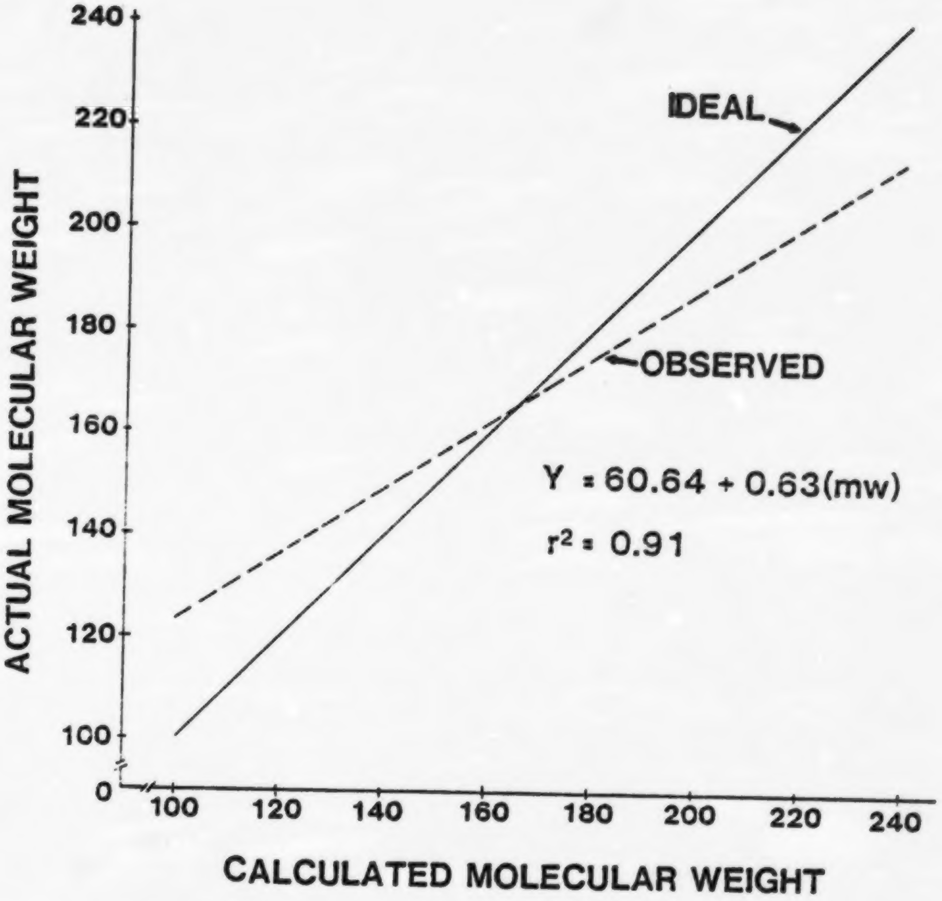


Figure 40. Regression analysis of predicted molecular weights for PS and that measured by mass spectral analysis.

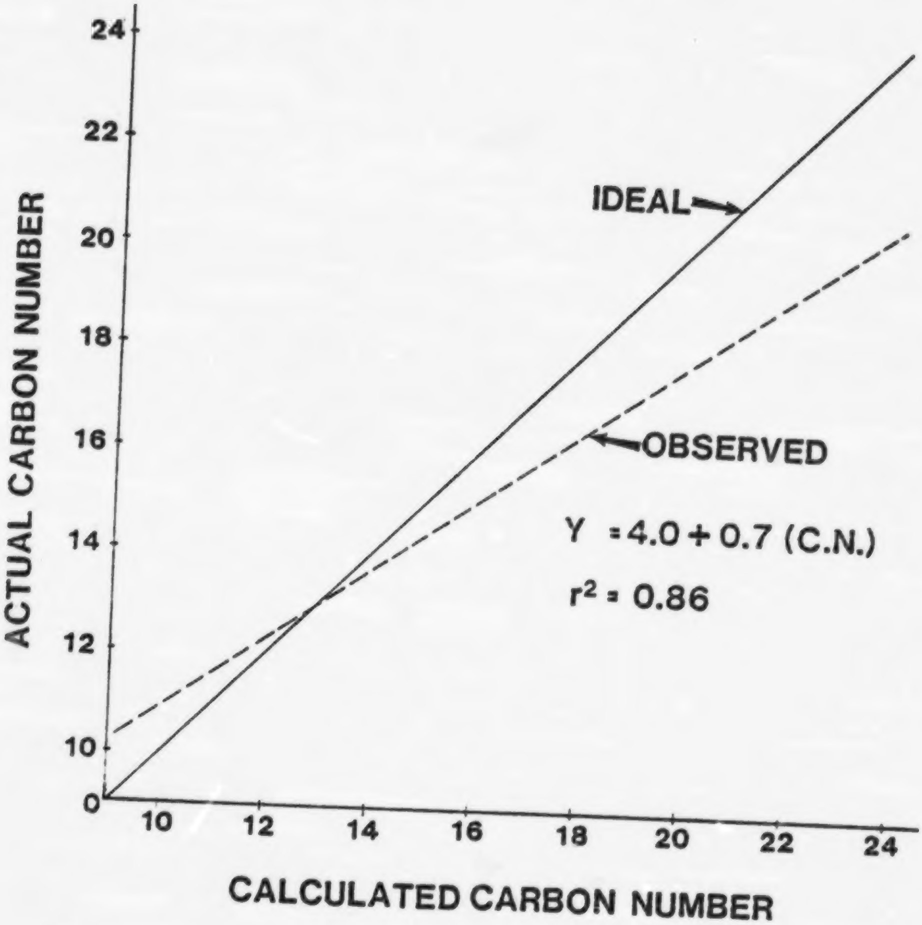


Figure 41. Regression analysis of predicted carbon numbers for PS and that estimated from probable structures determined by mass spectral analysis.

Actual MW and CN of PS materials in combined Fractions 2 and 3 were correlated against GLC retention times using a linear regression model. The equations and regression coefficient are given below:

$$\text{Molecular Weight} = 108.5 + 2.5\ (\text{RT}) \quad r^2 = 0.90$$

$$\text{Carbon Number} = 8.4 + 0.19\ (\text{RT}) \quad r^2 = 0.86$$

The equations obtained are useful in describing characteristics of PS materials chromatographed but not resolved as peaks.

The RT corresponding to the apex of the conical area under the peaks eluted for combined Fractions 2 and 3 was 37.2 minutes (Figure 37). The apex (assumed to correspond to the greatest bulk material elution rate from the GC column) for Fraction 4 occurs at approximately 57.2 minutes. The apex was determined as the point of intersection for straight lines drawn asymptotic to the baseline described for the peaks. By inserting the retention times into the above equations, the molecular weight and carbon numbers corresponding to the bulk elution of materials not resolved as peaks can be calculated. Resultant MW and CN for combined Fractions 2 and 3 was 201 g/mole and 15 carbon units, respectively. Fraction 4 gave a bulk MW of 251 g/mole and CN of 19. Based on the procedural paper and the differing principles of column chromatography, one would expect higher molecular weight aromatics in Fraction 4.

Summary of Waste Characterization Scheme

The RS material contained approximately 10% extractable hydrocarbons distributed as 60% saturates and 40% aromatic in character. Eighty-six percent of the carbon value assayed by wet combustion technique was quantitated by GLC, standarized to a carbon response. Nearly 80% of the total extracted hydrocarbons were recovered following fractionation on silica gel. The saturate fraction was characteristically 88% carbon. No attempt was made to characterize the aromatic fraction of the RS, other than by GLC analysis.

The PS material contained 62% extractable hydrocarbons assayed gravimetrically. Some 28% of the whole waste extractable hydrocarbon was quantitated by GLC as carbon, which corresponds to approximately 67% of the carbon assayed by wet combustion technique. Approximately 88% of the hydrocarbons extracted were recovered from silica gel. Combined silica gel Fractions 2 and 3 contained 96% of the extractable hydrocarbons recorded. GLC and GC-mass spectral analyses showed the extracted materials to be a complex mixture of relatively low molecular weight aromatics. A significant portion of the PS was not extractable, but decomposed thermally at 750 C. The utility of column fractionation in combination with GLC analysis was demonstrated for characterizing whole extracts from complex waste streams. Characterization stems from the GLC profiles developed for the various fractions and material quantitated as carbon.

Characterization of the Receiving Soils

Soils were selected to give a diverse range in both chemical and physical properties. The range in characteristics, while not all encompassing, does reflect some of the variability of soils within the continental United States.

Chemical and physical properties for the soils chosen are summarized in Tables 35 through 38. Soil taxonomic delinations reflect series names as mapped by the Soil Conservation Service (SCS). Soil properties do not always correspond to SCS mapping units due to man-made or natural changes in profile properties. The Nacogdoches soil (Rhodic Paleudalf) was sampled from an area mapped as such, but properties shown in Table 35 do not reflect the typical profile. Chemical properties (Table 35A) show it to be an acidic soil with a base status ranging between 58% in the surface 0-25 cm to less than 40% in the lower profile.

TABLE 35A. CHEMICAL PROPERTIES OF THE NACOGDOCHES SOIL SERIES

			Exchangeable Cations		
Depth (cm)	pH	CEC* (meq/100g)	Ca^{++}	Mg^{++} meq/100g	K^{+}
0.0-25.4	5.59	17.2	6.4	3.3	0.4
25.4-50.8	5.50	25.1	6.4	3.3	0.4
50.8-91.5	5.68	31.6	6.4	3.3	0.4
91.5-152.0	5.75	38.0	6.4	3.3	0.4
152.0-183.0	5.69	24.6	6.4	3.3	0.4

* CEC = cation exchange capacity.

TABLE 35B. PHYSICAL PROPERTIES OF THE NACOGDOCHES SOIL SERIES

Depth (cm)	Texture (USDA)	Particle Distribution Sand	Silt	Clay
		---------------	%	---------------
0.0-25.4	c	41.8	12.9	45.3
25.4-50.8	c	20.2	11.3	68.5
50.8-91.5	c	14.3	10.0	75.7
91.5-152.0	c	13.5	10.3	76.2
152.0-183.0	c	9.9	11.4	78.7

These values are within reason; however, textural data (Table 35B) suggests that the sandy loam surface was eroded exposing the more clayey subhorizons. The typical alfisol texture discontinuity between surface and subhorizons is therefore not evidenced from the data presented. However, there is greater than a 20% increase in clay content between the surface 0-25 cm and adjacent 25-50 cm depth interval. Since this is typical of the difference in clay contents between surface and subsurface horizons of alfisols, the soil was deemed acceptable for this study.

Lakeland soil (Typic Quartzipsamment) was taken from an area previously mapped and classified by the SCS. Chemical properties (Table 36A) reflect the slight acidity and low

TABLE 36A. CHEMICAL PROPERTIES OF THE LAKELAND SOIL SERIES

Depth (cm)	pH	CEC* (meq/100g)	Exchangeable Cations Ca^{++}	Mg^{++}	K^{+}
			--------	meq/100g	-------
0.0-15.2	6.45	0.3	3.0	0.8	0.5
15.2-30.5	6.13	0.61	3.0	0.8	0.5
30.5-60.1	5.96	2.05	3.0	0.8	0.5
60.1-91.5	5.83	-	3.0	0.8	0.5
91.5-122.0	6.13	-	3.0	0.8	0.5
122.0-152.0	6.29	1.31	3.0	0.8	0.5

* CEC = cation exchange capacity.

cation exchange capacity (CEC) typical of this mapping unit. Textures show the soil to be a sandy loam material throughout the profile. This soil is freely permeable to water and is never saturated.

The Norwood soil (Typic Udifluvent) is shown to have a basic soil reaction and CEC of approximately 20 throughout the profile, with the exception of a lens of material 119-112 cm that has a CEC of 30 (Table 37A). Textural analyses show two clay zones (Table 37B). The zone at 30.5-61 cm is approximately 10% higher in clay than the upper 20cm of soil, while the zone between 119-122 cm is 20% higher in clay than the preceeding zone.

TABLE 36B. PHYSICAL PROPERTIES OF THE LAKELAND SERIES

Depth (cm)	Texture (USDA)	Particle Distribution		
		Sand	Silt	Clay
			%	
0.0-15.2	sl	81.1	4.5	14.4
15.2-30.5	sl	80.6	2.5	16.9
30.5-61.0	sl	80.2	4.3	15.5
61.0-91.5	sl	81.3	4.1	14.7
91.5-122.0	sl	80.2	4.8	15.0
122.0-152.0	sl	80.9	4.1	15.0

TABLE 37A. CHEMICAL PROPERTIES OF THE NORWOOD SOIL SERIES

Depth (cm)	pH	CEC* (meq/100g)	Exchangeable Cations		
			Ca^{++}	Mg^{++}	K^{+}
				meq/100g	
0.0-15.2	7.69	19.6	20	4.0	0.8
15.2-30.5	7.73	21.1	20	4.0	0.8
30.5-61.0	7.74	22.9	20	4.0	0.8
61.0-91.5	7.86	17.8	20	4.0	0.8
91.5-119.0	7.75	16.2	20	4.0	0.8
119.0-122.0	7.75	30.0	20	4.0	0.8
122.0-152.0	7.95	13.2	20	4.0	0.8

* CEC = cation exchange capacity.

Chemical properties of the Bastrop soil (Udic Paleustalf) are given in Table 38A. Although the surface 0-15 cm is moderately acidic, the general profile does not reflect a significant acidic reaction, commensurate with the decreasing base status with depth to the 122 cm zone. Alfisols characteristically have base status percentages (sum of exchangeable cations divided by CEC) less than 50% and greater than 35%. Many alfisols will have alkaline subhorizons such as noted for the 122-152 cm depth interval. Physical data shown in Table 38B reflect a distinct textural discontinuity (abrupt increase in clay) between the 0-15.2 cm and 15.2-30.5 cm depth increments typical of an alfisol.

TABLE 37B. PHYSICAL PROPERTIES OF THE NORWOOD SOIL SERIES

Depth (cm)	Texture (USDA)	Particle Distribution Sand	Silt	Clay
		---------	%	---------
0.0-15.2	sc	48.2	15.2	36.6
15.2-30.5	scl	49.6	15.1	35.3
30.5-61.0	c	36.0	18.4	45.6
61.0-91.5	cl	40.5	22.3	37.2
91.5-119.0	cl	42.0	25.0	33.0
119.0-122.0	c	23.1	20.5	55.6
122.0-152.0	scl	49.1	15.8	35.1

TABLE 38A. CHEMICAL PROPERTIES OF THE BASTROP SOIL SERIES

Depth (cm)	pH	CEC* (meq/100g)	Exchangeable Cations Ca^{++}	Mg^{++}	K^{+}
			--------	meq/100g	-------
0.0-15.2	5.6	27.4	14.6	3.2	0.5
15.2-30.5	6.4	34.7	14.6	3.2	0.5
30.5-61.0	6.4	38.6	14.6	3.2	0.5
61.0-91.5	6.9	39.2	14.6	3.2	0.5
91.5-119.0	7.1	34.5	14.6	3.2	0.5
119.0-122.0	7.1	20.4	14.6	3.2	0.5
122.0-152.0	7.95	13.2	20	4.0	0.8

* CEC = cation exchange capacity.

TABLE 38B. PHYSICAL PROPERTIES OF THE BASTROP SOIL SERIES

Depth (cm)	Texture (USDA)	Particle Distribution		
		Sand	Silt	Clay
			%	
0.0-15.2	scl	60.3	10.0	29.7
15.2-30.5	c	39.8	12.6	47.6
30.5-61.0	c	36.5	11.5	52.0
61.0-91.5	c	33.2	12.0	54.8
91.5-122.0	c	35.4	10.8	53.8
122.0-152.0	scl	58.1	5.6	36.3

TABLE 39. PERCENT WASTE EXTRACTED FROM SPIKED SOILS RELATIVE TO SLUDGE SOURCE AND EXTRACTION TECHNIQUE

	Percent Waste Extracted*			
	Refinery		Petrochemical	
	Soxhlet	Blended	Soxhlet	Blended
None	9.92	9.81	62.00	58.11
Lakeland	9.85	9.42	60.58	58.89
Nacogdoches	9.37	10.54	58.12	54.71
Bastrop	9.54	10.22	60.60	57.34
Norwood	9.67	10.95	57.41	51.62
Avg.	9.67	10.19	59.74	56.13

* Hydrocarbons extracted were assayed gravimetrically.

Extraction of Waste from Soil

Soxhlet and blender techniques for extracting sludge materials from soil are compared in Table 39. Percent waste extracted was calculated based on the 10 g wet weight loading. Soxhlet and blended samples were both extracted with 15% diethylether in dichloromethane.

An analysis of variance of the data presented indicated that the blending technique was just as efficient in extracting hydrocarbons from sludge-soil mixtures as the more laborious Soxhlet technique. Differences in the quantities extracted between soils was not statistically significant. As one would expect, differences between sludge sources were highly significant.

DEGRADATION AND MOBILITY

Refinery Sludge

A 5% (w/w) refinery sludge application was made to duplicate soils contained in field installed lysimeters. Theoretically the loading rate is equivalent to 2,340 ppm extractable hydrocarbons that can be detected as carbon. Although, the application was made by hand mixing with the surface 15 cm of soil, it should be noted that the natural structure associated with peds and clods of field soil work against achieving a homogenous mixture. More realistically, the application rate is best described as a range between 1,730 and 3,440 ppm carbon, calculated on the basis of an estimated ±30% soil mass error.

Subsequent GLC analyses of the first samples taken following the sludge application pointed to the need for managing the variability due to sampling error. Because of the long-term nature of the field experiment, it was decided to combine cores from duplicate lysimeters to obtain a larger sample rather than punch more cores. Composites were therefore made in the laboratory and mixed by hand prior to subsampling for solvent extraction and GC analysis of column fractions. This negated the natural variability between duplicate lysimeters but provided better estimates of extractable hydrocarbons relative to waste source, time, and depth interval. The results of the total hydrocarbons assayed for field samples following the application of refinery sludge are summarized in Tables 40, 41, 42 and 43 for the Nacogdoches, Lakeland, Norwood and Bastrop soils, respectively. A control sample profile reflecting the innate hydrocarbon levels by fraction and depth increment was taken just prior to the sludge application. This demonstrated the relatively low extractable hydrocarbon level initially within the profiles.

Subsequent samples relative to application dates and other management practices are summarized in the activities schedule (Table 25). Scheduled events show that only one of the two lysimeters for each soil received a second and third application of sludge. Depth intervals were still combined

TABLE 40. DISTRIBUTION OF HYDROCARBONS CHROMATOGRAPHED FOR NACOGDOCHES SOIL

Depth (cm)	Fraction	Control	Sampling Dates					
			4/18/79	6/25/79	9/26/79	12/31/79	3/26/80	7/16/81
0-15	1	2.7	301.1	664.0	64.8	160.0	86.6	55.7
	2&3	0.8	334.9	95.8	65.8	189.3	31.4	49.9
	4	15.5	1.1	45.4	11.4	41.3	16.6	0.2
	Total	19.0	637.1	805.2	142.0	390.6	134.6	105.8
15-30	1	19.0	319.5	376.4	131.2	78.3	79.4	9.7
	2&3	0.4	185.0	114.8	15.3	16.1	67.2	10.9
	4	3.3	22.0	178.8	0.9	0.2	0.2	11.4
	Total	22.7	526.5	670.0	147.4	94.6	146.8	32.0
30-45	1	9.5	245.0	18.2	88.3	126.1	41.5	16.2
	2&3	4.1	292.8	31.5	22.4	33.0	26.5	14.1
	4	0.2	33.5	0.5	0.2	4.6	0.9	21.4
	Total	13.8	571.3	50.2	110.9	163.7	68.9	51.7
45-90	1	205.5	212.5	130.1	0.7	28.8	0.5	15.1
	2&3	0.3	19.3	38.3	0.6	28.3	7.2	15.3
	4	0.2	0.2	0.2	0.4	5.0	1.0	12.7
	Total	206.0	232.0	168.6	1.7	62.1	8.7	43.1
90-150	1	64.2		25.4	4.5	47.8	8.7	152.9
	2&3	2.8		2.8	1.9	15.1	0.2	37.0
	4	0.2		0.6	0.1	1.2	0.5	11.2
	Total	67.2		28.8	6.5	64.1	9.4	201.1

TABLE 41. DISTRIBUTION OF HYDROCARBONS CHROMATOGRAPHED FOR LAKELAND SOIL

Depth (cm)	Fraction	Control	Sampling Dates 4/18/79	6/25/79	9/26/79	12/13/79	3/26/79	7/16/81
0-15	1	7.8	443.9	169.5	25.2	67.1	86.2	34.3
	2&3	16.7	103.3	235.4	42.8	317.0	79.0	23.9
	4	6.8	66.0	28.9	22.7	50.6	24.9	6.7
	Total	31.3	616.2	433.8	90.7	434.7	190.1	64.9
15-30	1	14.6	224.3	72.4	18.0	107.3	45.9	35.7
	2&3	0.2	153.0	47.6	23.4	222.5	41.1	8.9
	4	0.2	41.8	14.9	13.7	32.3	9.7	6.7
	Total	15.0	419.1	134.9	55.1	362.1	96.7	51.3
30-45	1	8.2	91.8	0.5	15.4	53.4	8.9	12.4
	2&3	0.2	70.5	0.2	32.5	62.7	12.4	8.8
	4	0.4	16.5	0.4	12.2	24.7	15.4	7.8
	Total	8.8	178.8	1.1	60.1	140.8	36.7	29.0
45-90	1	14.0	166.9	10.4	12.3	31.3	45.7	26.5
	2&3	27.1	22.7	4.3	6.9	58.6	16.7	2.3
	4	5.4	82.6	0.2	42.4	10.4	12.6	0.9
	Total	46.5	272.2	14.9	61.6	100.3	75.0	29.7
90-150	1	0.2	33.0	12.7	9.0	9.7	87.9	1.5
	2&3	0.2	41.0	51.5	19.0	23.0	8.5	1.4
	4	1.4	10.0	43.7	20.4	86.9	28.8	0.2
	Total	1.8	84.0	107.9	48.4	119.6	125.2	3.1

TABLE 42. DISTRIBUTION OF HYDROCARBONS CHROMATOGRAPHED FOR NORWOOD SOIL

Depth (cm)	Fraction	Control	Sampling Dates					
			4/18/79	6/25/79	9/26/69	12/31/79	3/26/80	7/16/81
0-15	1	47.1	1,534.0	93.3	45.3	381.8	176.4	149.8
	2&3	0.2	697.6	94.8	110.4	252.7	81.1	55.3
	4	26.9	64.7	33.7	4.7	75.0	0.3	27.8
	Total	74.2	2,296.3	221.8	160.8	639.2	257.8	232.9
15-30	1	45.6	962.0	28.6	30.6	106.7	52.5	5.8
	2&3	8.0	413.2	56.9	390.8	83.2	52.4	7.6
	4	19.6	144.4	14.0	15.1	64.6	71.1	4.5
	Total	73.2	1,519.6	99.5	436.5	254.5	176.0	17.9
30-45	1	14.4	640.0	14.7	25.2	676.8	150.7	25.4
	2&3	0.2	36.1	40.6	40.1	1,208.6	89.2	8.7
	4	20.4	37.3	99.4	10.6	279.8	8.1	4.9
	Total	35.0	713.4	154.7	75.9	2,165.2	248.0	39.0
45-90	1	21.4	103.7	21.6	18.3	239.2	108.4	32.2
	2&3	4.8	49.5	10.4	26.7	174.9	124.9	23.6
	4	4.4	11.3	43.5	9.2	77.6	18.1	7.9
	Total	30.6	164.5	75.5	54.2	491.7	251.4	63.7
90-150	1	1.8		30.9	14.3	48.3	124.2	22.6
	2&3	0.2		4.8	19.9	86.0	28.3	21.1
	4	0.2		6.9	6.2	58.4	14.8	5.5
	Total	2.2		42.6	40.4	192.7	167.3	49.2

TABLE 43. DISTRIBUTION OF HYDROCARBONS CHROMATOGRAPHED FOR BASTROP SOIL

Depth (cm)	Fraction	Control	Sampling Dates 4/18/79	6/25/79	9/26/79	3/26/80	7/16/81
0-15	1	107.3	160.0	315.8	613.8	372.1	230.5
	2&3	26.8	333.3	197.5	305.3	182.9	100.4
	4	0.2	0.1	2.1	39.9	0.1	0.1
	Total	134.3	493.4	515.4	959.0	555.1	331.0
15-30	1	43.9	359.9	106.1	106.1	162.2	70.3
	2&3	24.8	31.6	59.8	66.3	76.4	60.7
	4	2.0	2.4	1.1	3.3	0.4	2.9
	Total	70.7	393.9	167.0	175.7	239.0	133.9
30-45	1	10.0	129.5	59.6	93.5	62.2	21.0
	2&3	37.2	74.1	23.0	50.3	36.0	10.0
	4	0.0	0.1	41.1	11.0	0.1	0.2
	Total	47.2	203.7	123.7	154.8	98.3	31.2
45-90	1	4.1	93.7	63.2	60.1	66.6	20.3
	2&3	10.1	1.9	36.7	52.5	27.4	12.6
	4	5.1	0.1	56.4	7.1	0.1	0.2
	Total	19.3	95.7	156.3	119.7	94.1	33.1
90-150	1	15.5	43.3	87.5	136.4	4.2	52.2
	2&3	5.7	14.9	50.8	47.6	13.8	8.7
	4	1.7	3.8	4.5	4.7	0.4	0.2
	Total	22.9	62.0	142.8	188.7	18.4	61.1

for extraction and analysis to improve the chances of seeing degradation products by increasing sample size. The exception was the 12-31-79 sampling date for which only the lysimeter receiving the second application was sampled.

Hydrocarbon distributions differentiated as saturates, aromatics, and totals relative to time are shown in Figures 42, 43, 44 and 45. Data points for saturates reflect the materials chromatographed in Fraction 1 summed over depth. Aromatics represent the materials chromatographed in Fractions 2, 3, and 4. These data shown clearly that refinery sludge is degraded following successive applications of refinery sludge (application denoted by arrow). Hydrocarbon values reflected at 42 and 54 weeks into the experiment correspond to the December and March sampling dates. Lower March values reflect a continued degradation of refinery sludge over the relatively mild winter months at College Station, Texas. Soil temperature taken in a lysimeter of Norwood soil at a depth of 6.4 cm was 10 C in December and 13 C at the March sampling date.

Hydrocarbon distributions summed over time are plotted against depth in Figures 46, 47, 48 and 49 for the Nacogdoches, Lakeland, Norwood, and Bastrop soils, respectively. Distributions generally correspond to soil physical properties in that increasing clay contents with depth retard the movement of refinery sludge within the profile. Migration of hydrocarbons out of the zone of incorporation was most pronounced in the coarse-textured Lakeland sand.

The proportions of saturates to aromatics are somewhat lower than reflected in the refinery sludge analysis. This was attributed to a greater degradation rate for saturate hydrocarbons.

Typical GLC profiles chromatographed for saturates contained in Fraction 1 (Figures 50A and 50B) and aromatics in combined Fractions 2 and 3 (Figure 51A and 51B) show that materials initially detected as peaks were rapidly dissipated. The bulk of materials chromatographed were quantitated as a conical area. Peak profiles at lower depths reveal the reflected waste characteristics, indicative of the migration of whole sludge materials. Materials which migrated out of the zone of incorporation were generally the lower molecular weight materials resolved as peaks. Material moving downward was eventually retained and most likely degraded in the oxidized soil even at lower depths within the profile. Analysis of leachate waters collected over the course of the 2 year field study revealed

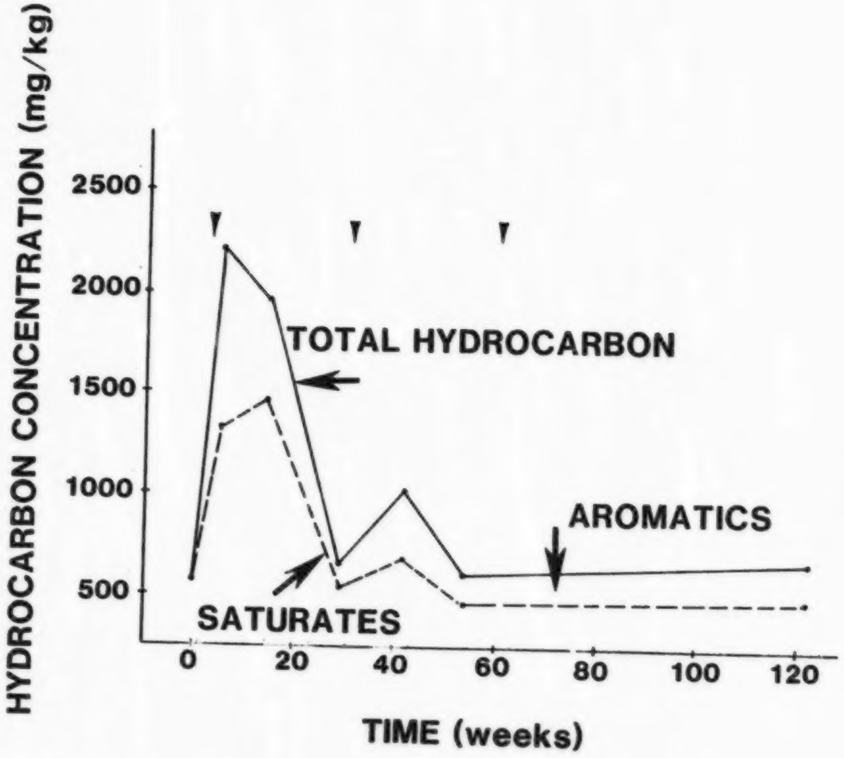


Figure 42. Hydrocarbon distribution with time for refinery sludge amended Nacogdoches soil.

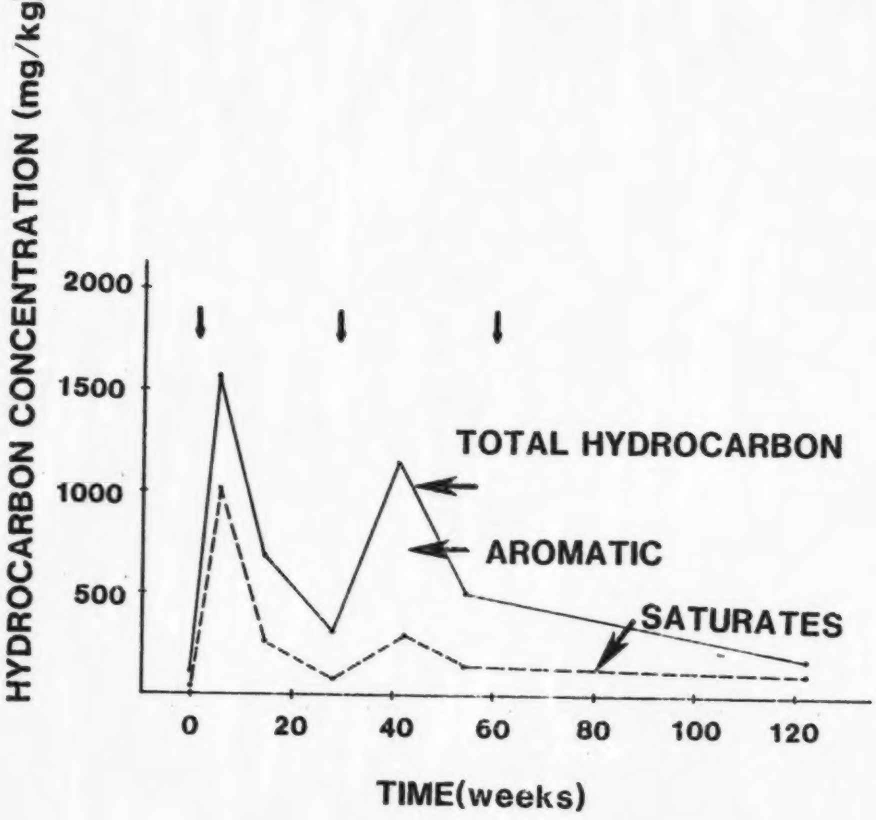


Figure 43. Hydrocarbon distribution with time for refinery sludge amended Lakedland soil.

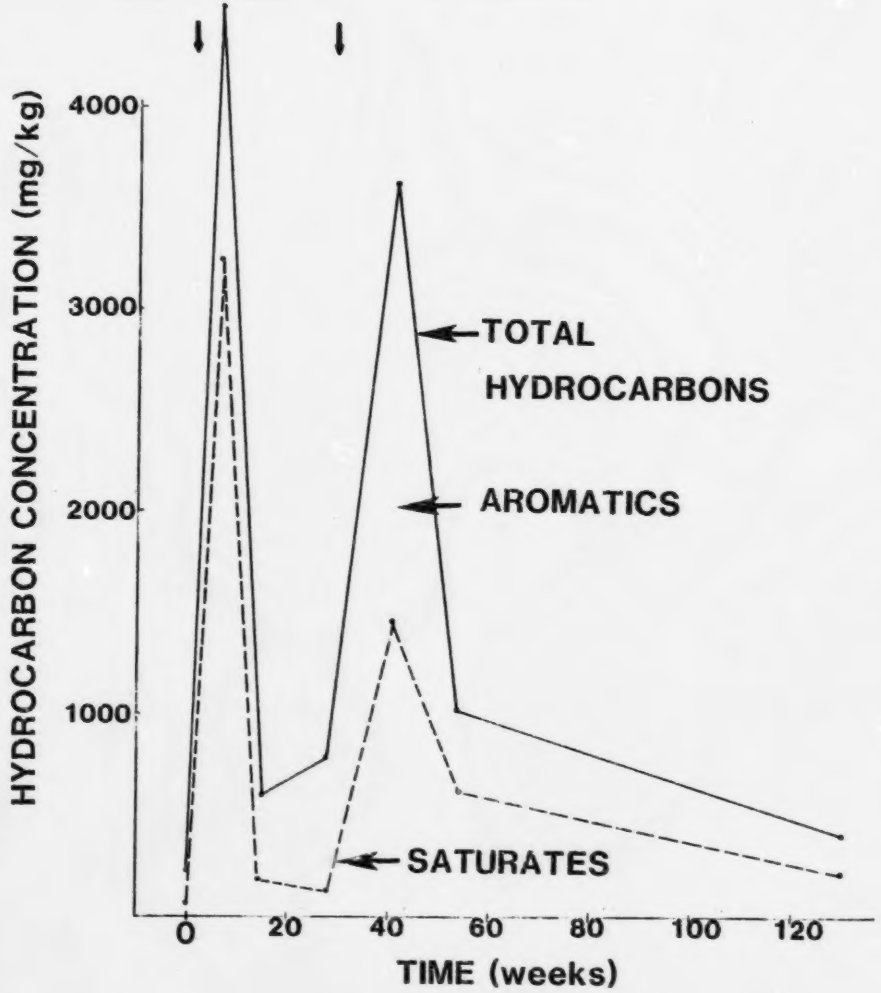


Figure 44. Hydrocarbon distribution with time for refinery sludge amended Norwood soil.

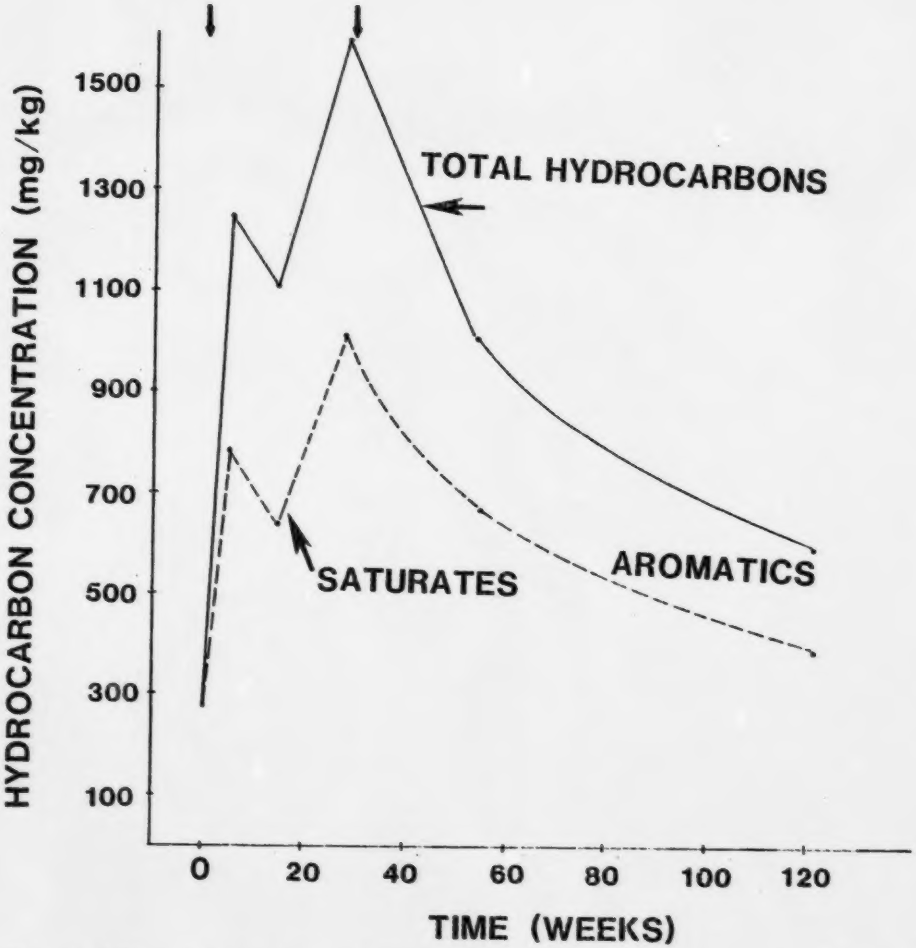


Figure 45. Hydrocarbon distribution with time for refinery sludge amended Bastrop soil.

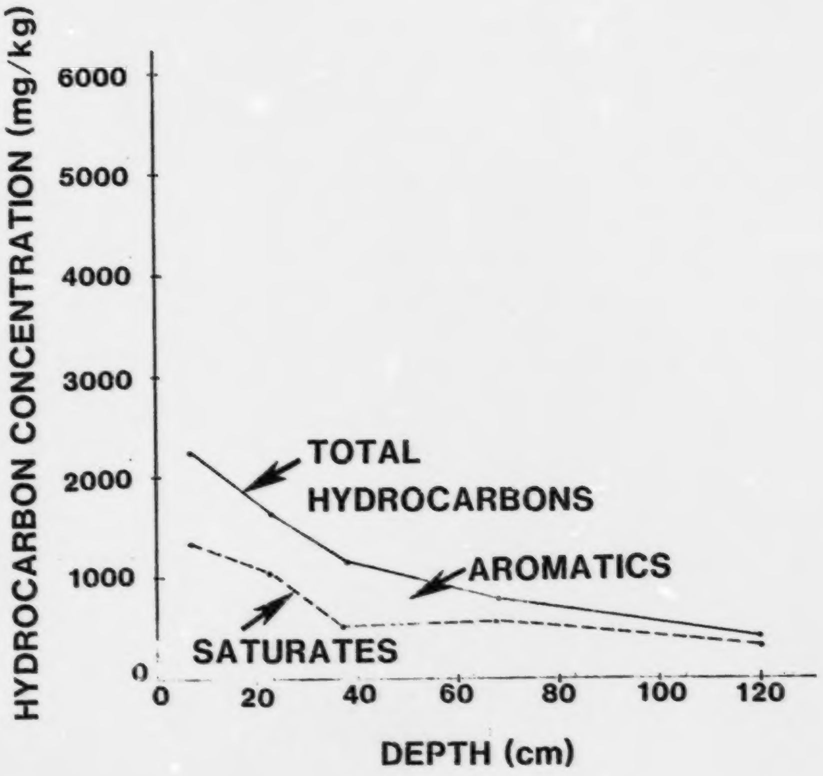


Figure 46. Hydrocarbon distribution with depth for refinery sludge amended Nacogdoches soil.

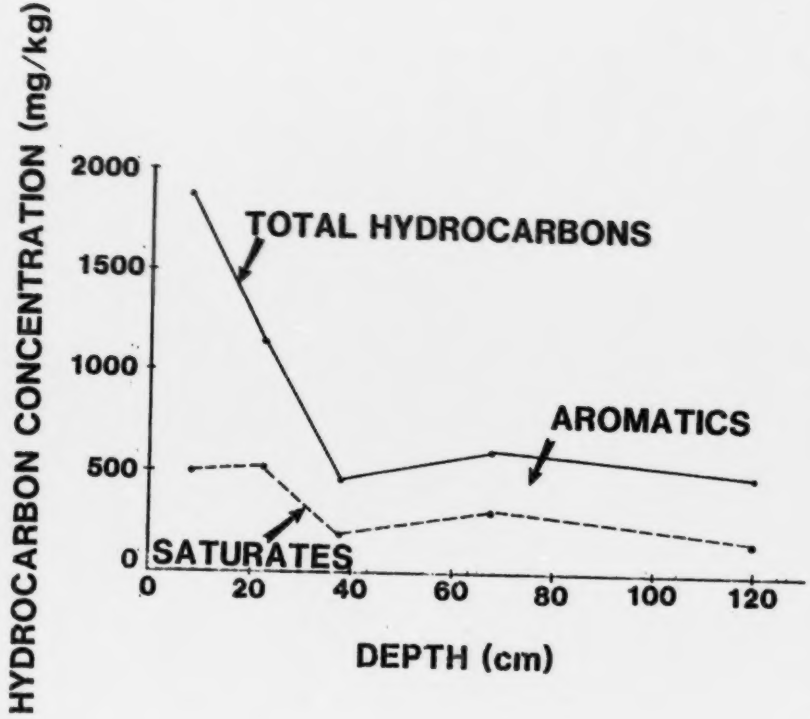


Figure 47. Hydrocarbon distribution with depth for refinery sludge amended Lakeland soil.

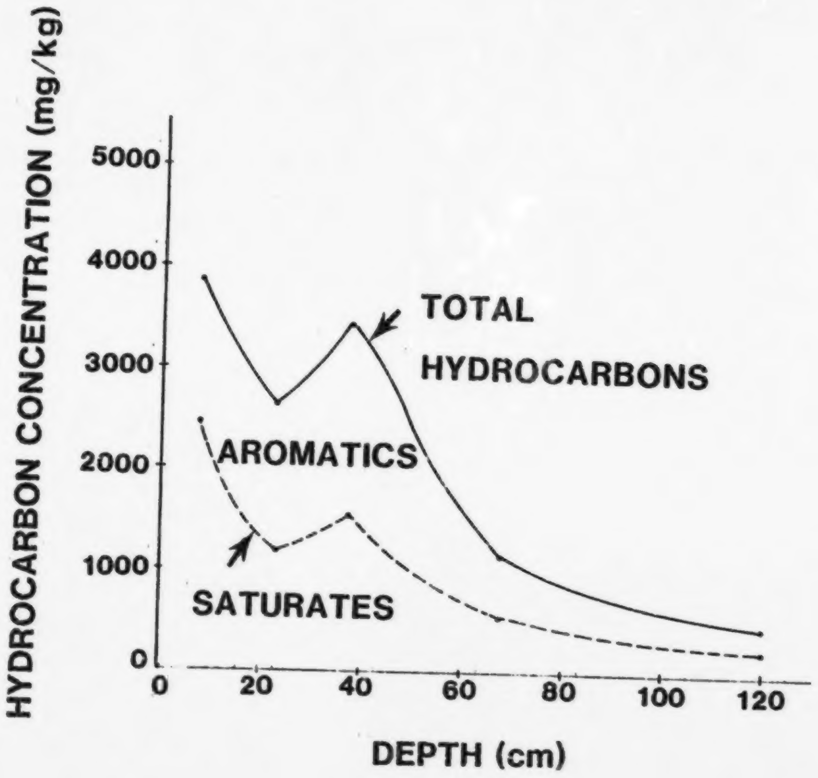


Figure 48. Hydrocarbon distribution with depth for refinery sludge amended Norwood soil.

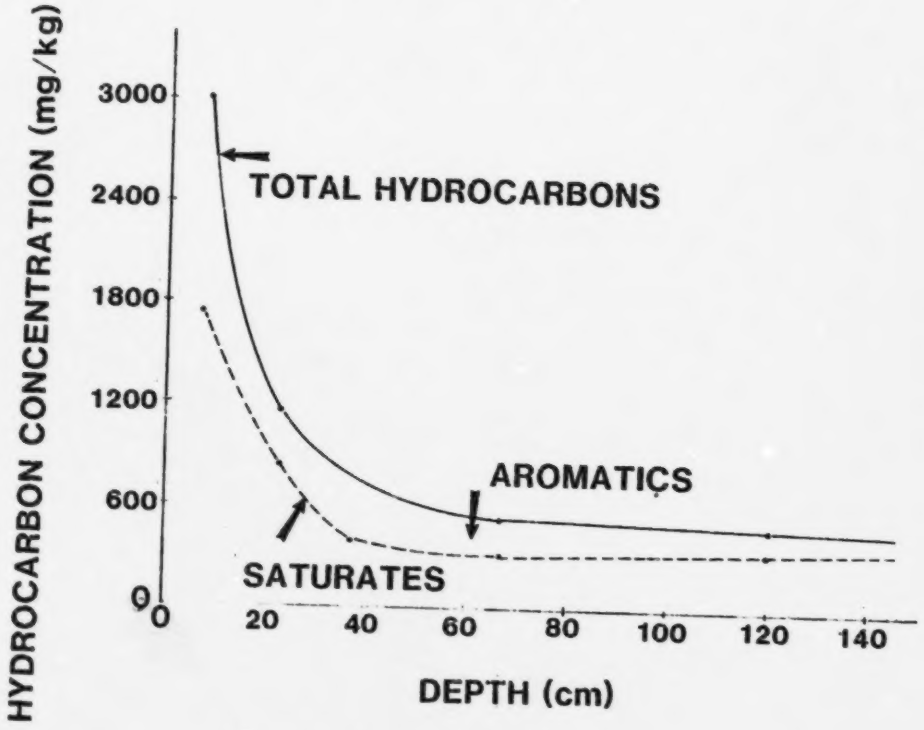


Figure 49. Hydrocarbon distribution with depth for refinery sludge amended Bastrop soil.

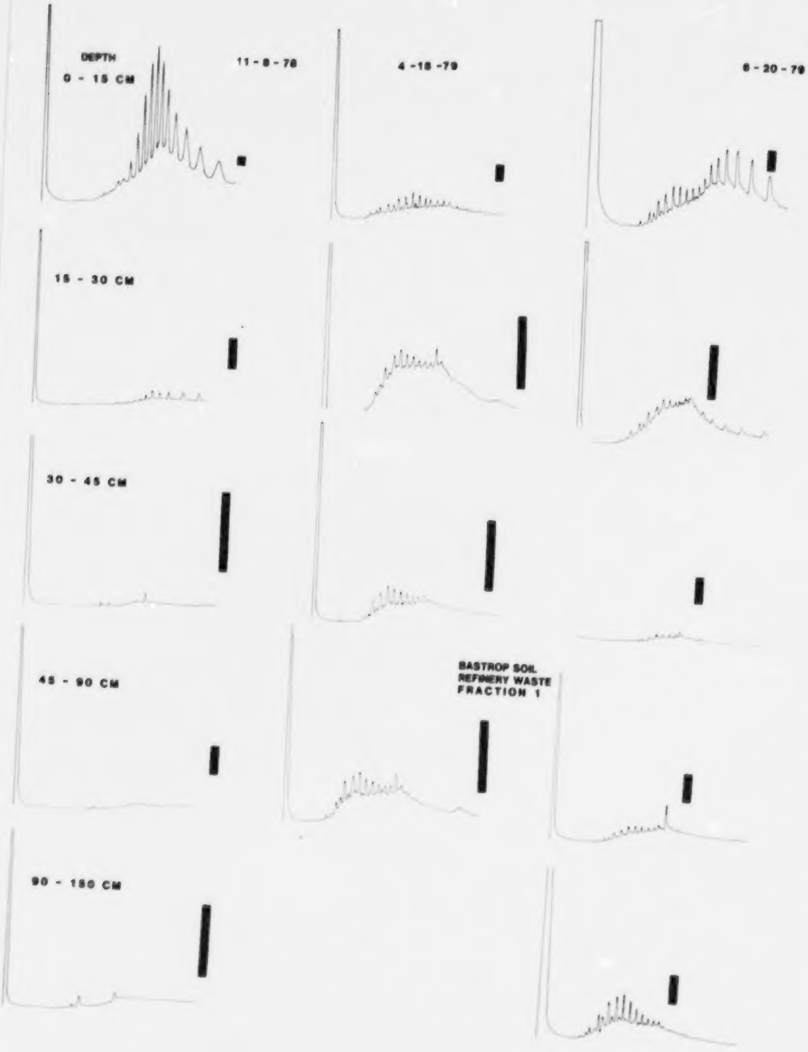


Figure 50A. GLC profile of fraction 1 with depth and time from Bastrop soil treated with refinery sludge.

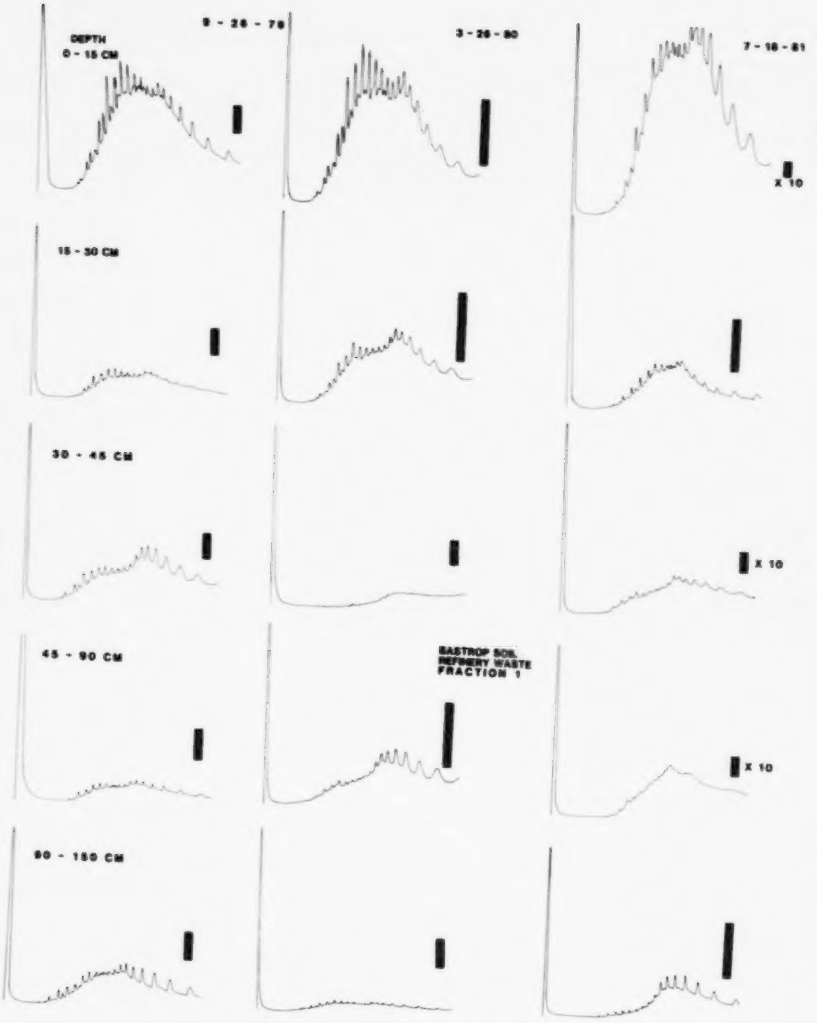


Figure 50B. GLC profile of fraction 1 with depth and time from Bastrop soil treated with refinery sludge.

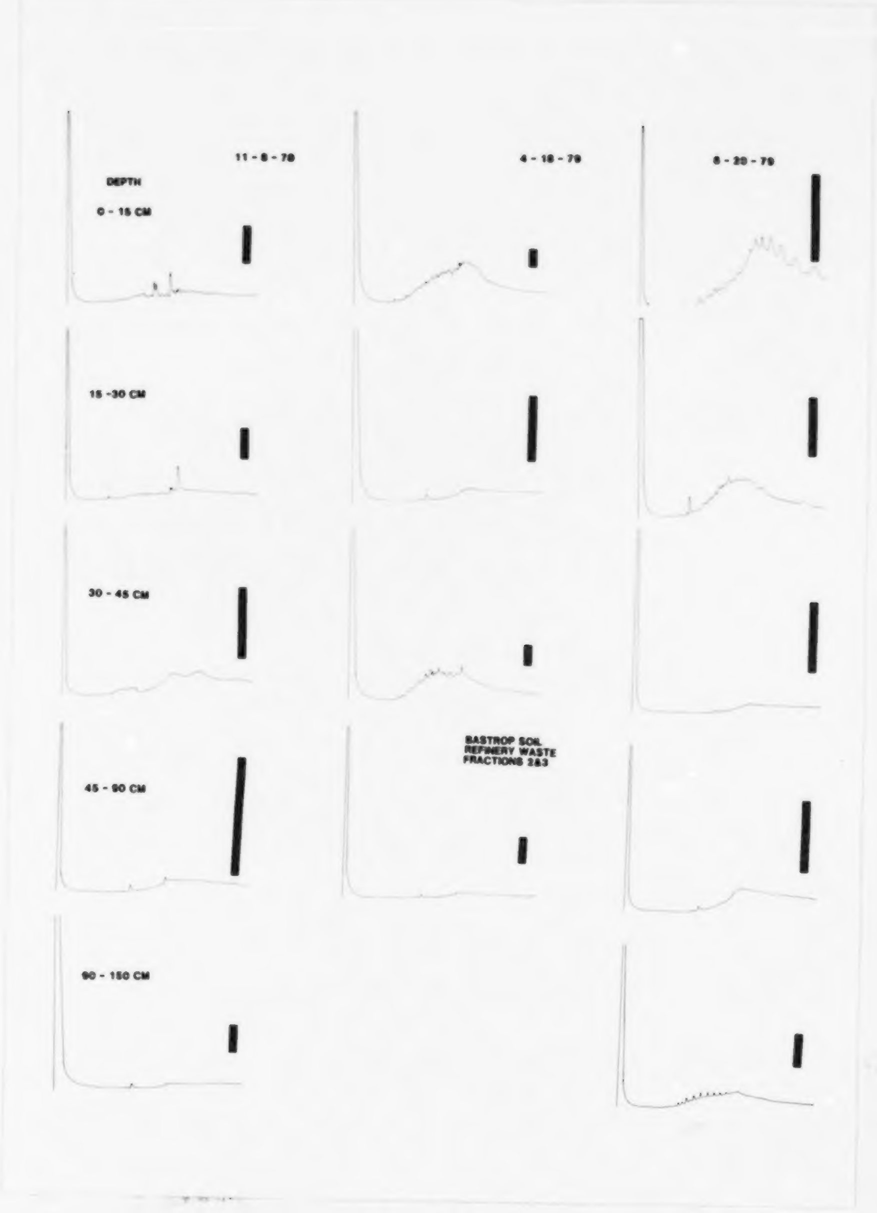


Figure 51A. GLC profile of fractions 2 and 3 with depth and time from Bastrop soil treated with refinery sludge.

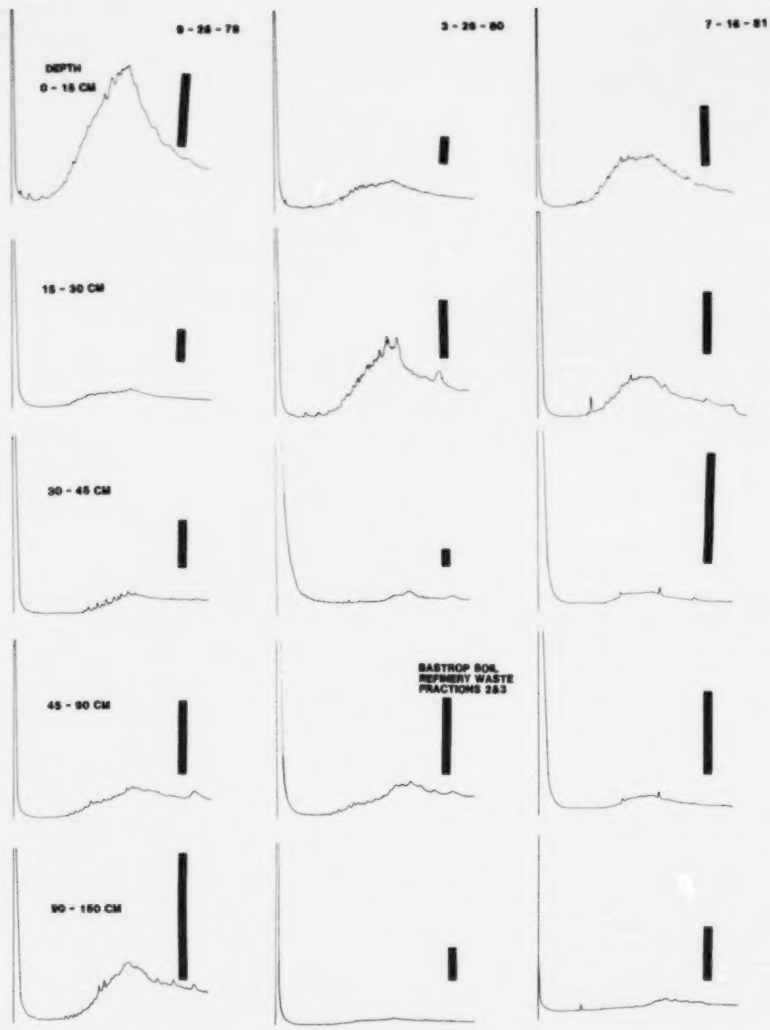


Figure 51B. GLC profile of fractions 2 and 3 with depth and time from Bastrop soil treated with refinery sludge.

that no whole refinery sludge was transmitted from the lysimeters at concentrations exceeding the detection limit of 1 ppm.

The combined effects of time and depth on total hydrocarbons chromatographed for the Bastrop soil amended with refinery waste sludge is shown in Figure 52. The latent peak shown for the surface horizon is attributed in part to breakdown products of naturally occurring soil humic materials (control - Table 43) and initial sampling errors. The diagram typifies the general distribution of refinery waste hydrocarbons added to the test soils with respect to time and depth of profile sampled.

Petrochemical Sludge

A 5% (w/w) petrochemical sludge application was made to duplicate soils contained in field installed lysimeters. The application corresponds to an extractable carbon loading of 9,000 μg/g within the zone of incorporation.

In addition, the Norwood soil lysimeter, and Bastrop soil lysimeter which had received only one previous application of petrochemical sludge were inadvertently treated with the refinery sludge on the April 30, 1980 application date (Table 25).

The results of the total hydrocarbons determined for field samples following the application of refinery sludge are summarized in Tables 44, 45, 46 and 47 for the Nacogdoches, Lakeland, Norwood, and Bastrop soils, respectively. The data show that the aromatic hydrocarbons chromatographed for Fractions 2 and 3 and Fraction 4 dominate the distribution of materials recovered with depth and time. Amounts recovered are exceedingly variable and point to the sampling error incurred. Part of the variability is attributed to the rapid degradation rate, particularly over the summer months.

Saturates and combined aromatic fractions totaled for the various depths within a sampling period are plotted in Figures 53, 54, 55 and 56. These curves serve to demonstrate the more rapid months. The significant penetration of sludge into the profile samples are demonstrated in the hydrocarbon levels totaled over time and plotted against depth (Figures 57, 58, 59 and 60).

Characteristic GLC profiles shown for Fraction 1 of the Bastrop soils, typify the relatively low saturate levels assayed for the petrochemical sludge amended soils (Figures

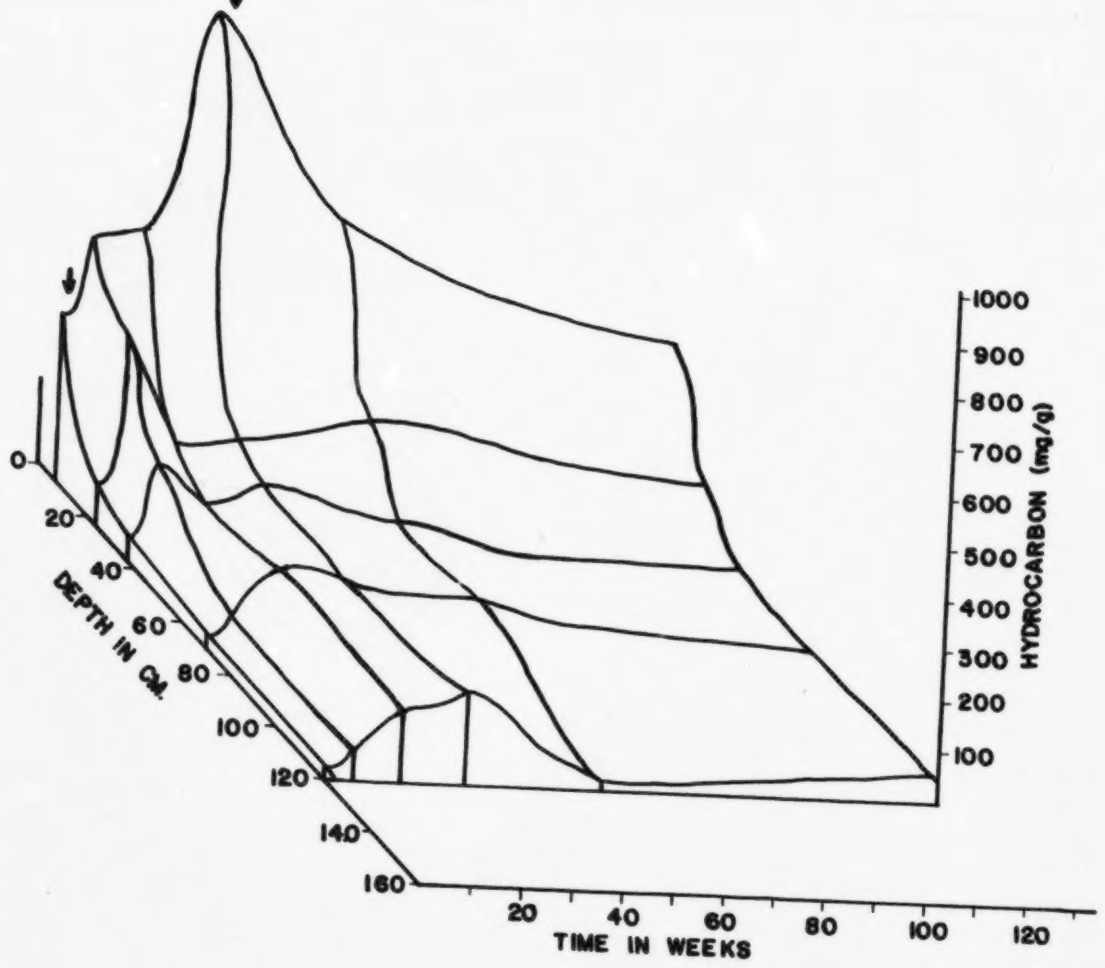


Figure 52. Hydrocarbon distribution with respect to time and depth for a Bastrop soil amended with refinery sludge.

TABLE 44. DISTRIBUTION OF HYDROCARBONS CHROMATOGRAPHED FOR NACOGDOCHES SOIL

Depth (cm)	Fraction	Control	Sampling Dates					
			4/18/79	6/25/79	9/26/79	12/31/79	3/26/80	7/16/81
0-15	1	2,537.0	106.2	163.5	55.1	65.8	230.1	37.5
	2&3	1,523.0	2,119.0	1,154.0	1,368.8	778.0	81.1	249.8
	4	57.2	78.6	421.6	32.1	16.7	11.5	69.9
	Total	4,117.2	2,361.1	1,739.1	1,456.0	860.5	322.7	357.2
15-30	1	25.3	78.0	268.4	1.2	26.3	129.7	6.3
	2&3	12.5	2,425.0	803.0	847.0	1,543.0	369.0	19.6
	4	0.9	116.0	41.4	22.7	18.5	11.8	0.2
	Total	38.7	2,619.0	1,112.8	870.9	1,587.8	510.5	26.1
30-45	1	0.2	79.1	98.1	0.2	6.6	11.2	18.2
	2&3	3.6	2,342.0	641.1	518.3	818.0	300.0	40.0
	4	1.2	130.3	10.9	33.2	17.1	14.5	3.8
	Total	5.0	2,551.4	750.1	551.7	841.7	325.7	62.0
45-90	1	7.5	39.3	40.7	0.4	14.4	23.2	29.4
	2&3	2.0	797.0	107.1	93.3	287.0	29.3	25.4
	4	0.2	133.5	1.9	31.7	17.8	10.0	0.5
	Total	9.7	969.8	149.7	125.4	319.2	62.5	55.3
90-150	1	175.0	53.2	7.1	9.6	6.6	16.1	10.0
	2&3	2.4	185.0	23.9	90.3	27.1	30.0	22.3
	4	51.4	8.9	21.0	14.8	47.9	17.9	5.3
	Total	228.8	247.1	52.0	240.1	81.6	6.4	37.6

TABLE 45. DISTRIBUTION OF HYDROCARBONS CHROMATOGRAPHED FOR LAKELAND SOIL

			Sampling Dates					
Depth	Fraction	Control	4/18/79	6/25/79	9/26/79	12/31/79	3/26/80	7/16/81
0-15	1	337.0	36.6	19.5	0.5	21.8	116.6	29.9
	2&3	110.1	2,779.1	2,363.0	425.6	1,996.0	568.4	706.0
	4	16.0	311.1	17.2	0.2	141.2	297.6	169.6
	Total	463.1	3,126.8	2,399.7	426.3	2,159.0	982.6	905.5
15-30	1	7.1	27.0	103.6	15.0	4.8	207.2	16.6
	2&3	5.7	460.5	387.7	102.3	205.8	955.8	187.4
	4	1.2	71.0	0.4	0.2	1,867.0	135.6	5.9
	Total	14.0	558.5	491.7	117.5	2,077.6	1,298.6	209.9
30-45	1	19.0	29.0	37.6	12.2	9.9	359.0	38.4
	2&3	5.4	242.4	93.5	349.2	653.0	384.0	28.7
	4	0.4	139.9	0.2	0.6	1.2	1.8	1.1
	Total	24.8	411.3	131.3	362.0	664.1	744.8	68.2
45-90	1	21.3	12.3	49.4	0.3	19.4	730.0	0.5
	2&3	0.8	26.4	61.7	119.0	1,232.0	266.0	36.2
	4	12.7	10.0	2.7	0.2	333.2	5.4	0.9
	Total	34.8	48.7	113.8	119.5	1,584.6	1,001.4	37.6
90-150	1	13.6	4.9	32.6	0.2	0.2	405.0	0.2
	2&3	0.6	6.9	80.6	29.8	219.6	278.6	5.7
	4	0.2	5.8	11.5	0.2	0.2	32.8	7.1
	Total	14.4	17.6	124.7	30.2	220.0	716.6	13.0

TABLE 46. DISTRIBUTION OF HYDROCARBONS CHROMATOGRAPHED FOR NORWOOD SOIL

Depth (cm)	Fraction	Control	Sampling Dates					
			4/18/79	6/25/79	9/26/79	12/31/79	3/26/80	7/16/81
0-15	1	17.5	30.0	34.1	136.7	191.3	60.2	263.6
	2&3	0.5	144.9	22.9	405.7	2,058.5	1,053.0	969.9
	4	39.4	49.1	0.2	71.5	1,046.0	124.0	239.4
	Total	57.4	174.9	57.2	613.9	3,295.8	1,237.2	1,472.9
15-30	1	45.0	107.4	0.5	22.3	360.2	60.9	40.0
	2&3	42.5	30.0	45.2	401.7	171.1	701.7	22.1
	4	133.7	11.4	10.9	99.9	64.0	123.0	11.2
	Total	221.2	148.8	56.6	523.9	595.3	885.6	73.3
30-45	1	147.1	1.5	0.2	38.2	9.6	96.8	14.9
	2&3	1,310.0	164.6	67.1	133.1	123.2	42.3	38.8
	4	5.0	15.3	7.1	0.2	74.1	137.0	18.1
	Total	1,462.1	181.4	74.4	171.5	206.9	276.1	71.8
45-90	1	63.5	177.0	4.7	74.5	50.9	51.4	35.8
	2&3	75.5	625.8	164.1	269.0	260.5	39.1	18.6
	4	139.0	121.3	1.1	58.0	147.4	31.1	13.3
	Total	278.0	923.3	169.9	401.5	458.8	121.6	67.7
90-150	1	0.5		141.9	0.2	0.2	0.3	20.0
	2&3	0.3		229.4	241.2	466.4	14.4	16.2
	4	0.8		1.2	12.5	19.4	2.0	1.0
	Total	1.6		372.5	253.9	486.0	16.7	37.2

TABLE 47. DISTRIBUTION OF HYDROCARBONS CHROMATOGRAPHED FOR BASTROP SOIL

Depth (cm)	Fraction	Control	Sampling Dates					
			4/18/79	6/25/79	9/26/79	12/31/79	3/26/80	7/16/81
0-15	1	10.8	4.1	16.5	23.9	97.9	91.6	55.6
	2&3	41.7	1,041.3	438.2	360.1	818.0	454.2	260.3
	4	12.4	171.5	29.3	21.3	370.6	13.1	115.8
	Total	64.9	1,216.9	484.0	405.3	1,286.5	558.9	431.7
15-30	1	6.4	1.8	2.7	3.4	96.2	15.1	34.0
	2&3	6.2	490.2	164.8	233.1	701.5	379.3	3.6
	4	7.3	0.2	31.7	10.6	35.3	32.0	1.5
	Total	19.9	492.2	199.2	247.1	833.0	426.4	39.1
30-45	1	4.3	15.8	1.3	10.1	19.2	5.8	1.1
	2&3	27.7	91.8	25.0	149.5	61.9	182.0	18.9
	4	5.5	8.0	0.2	5.6	15.5	1.9	1.2
	Total	37.5	115.6	26.5	165.2	96.6	25.9	21.2
45-90	1	14.4	12.6	8.7	6.3	14.8	25.6	6.4
	2&3	6.6	8.0	24.8	47.0	90.1	65.3	8.8
	4	11.6	0.9	19.9	1.1	97.9	5.8	1.1
	Total	33.0	21.5	53.4	54.4	202.8	96.7	16.3
90-150	1	0.5	5.7	6.4	10.9	5.5	10.4	0.5
	2&3	0.2	4.6	9.9	11.6	34.1	24.1	28.9
	4	7.8	10.1	18.3	13.6	11.2	5.1	2.3
	Total	8.5	20.4	34.6	36.1	50.8	39.6	31.7

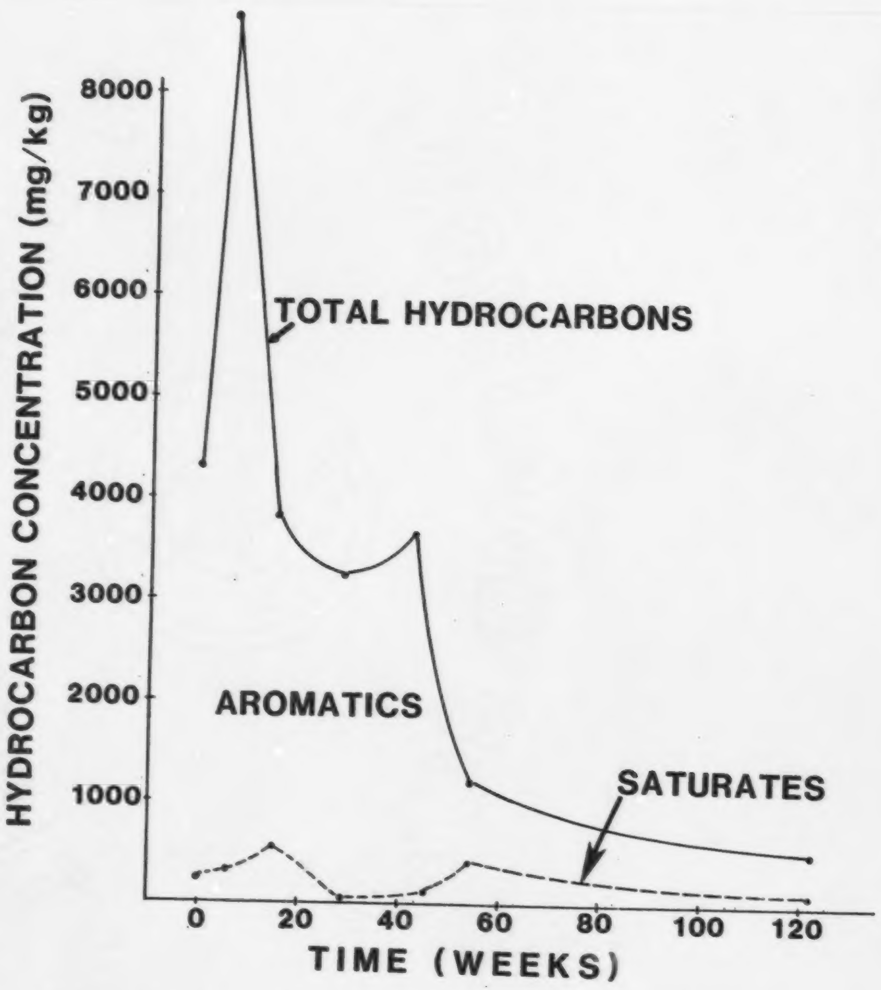


Figure 53. Hydrocarbon distribution with time for petrochemical sludge amended Nacogdoches soil.

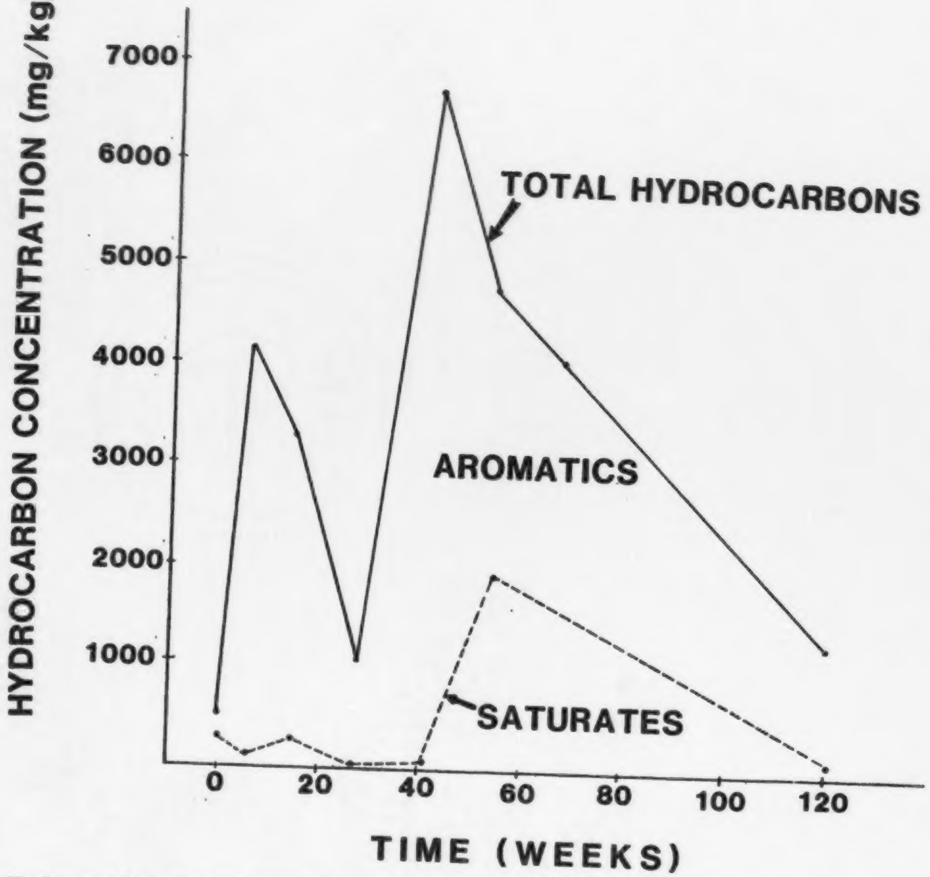


Figure 54. Hydrocarbon distribution with time for petrochemical sludge amended Lakeland soil.

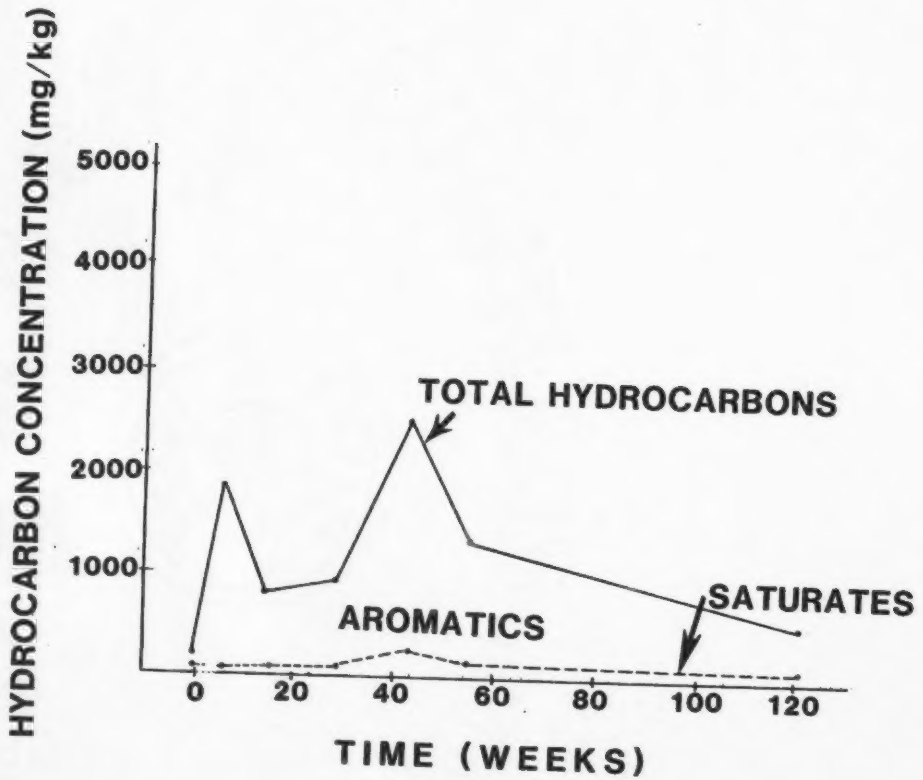


Figure 55. Hydrocarbon distribution with time for petrochemical sludge amended Bastrop soil.

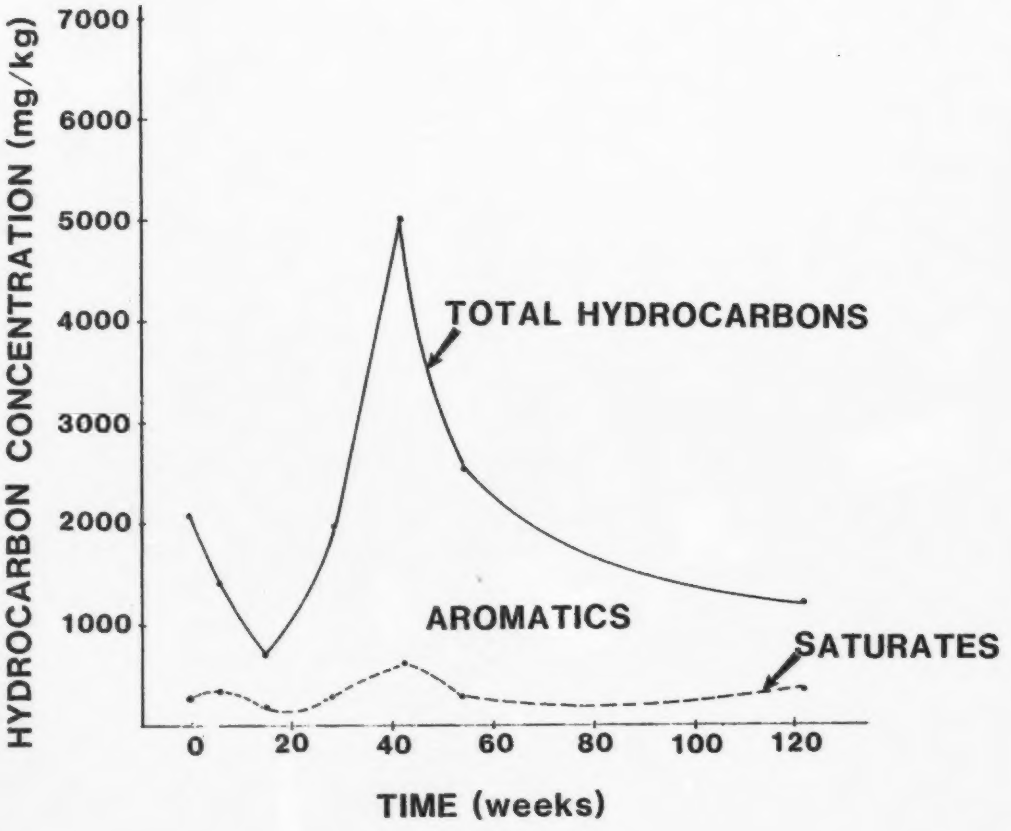


Figure 56. Hydrocarbon distribution with time for petrochemical sludge amended Norwood soil.

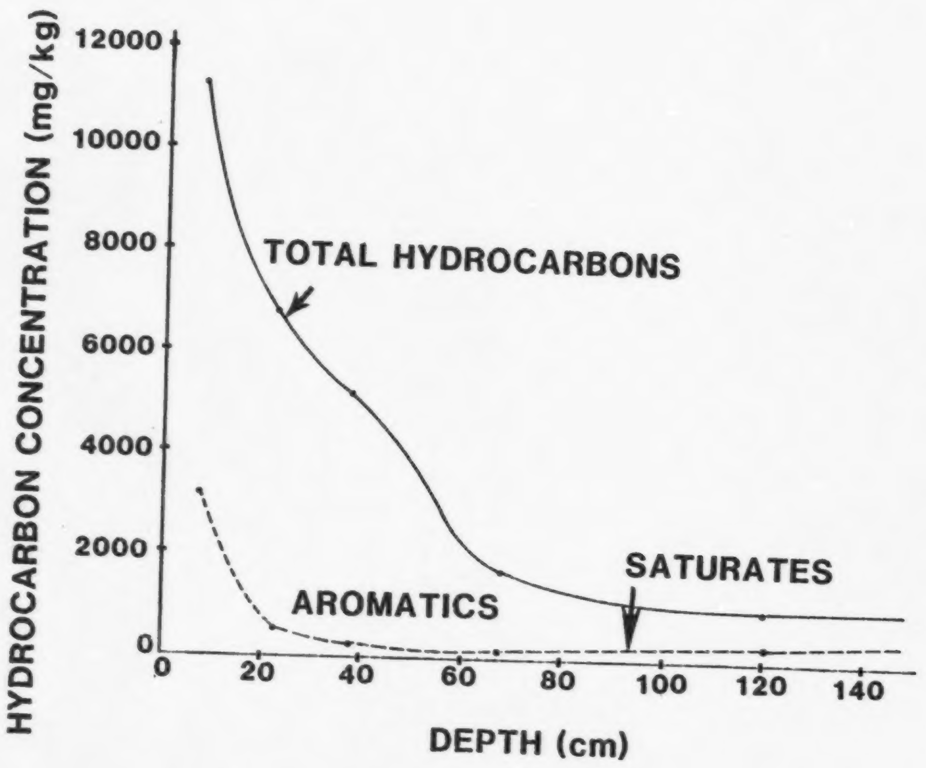


Figure 57. Distribution of hydrocarbons with depth for Nacogdoches soil amended with petrochemical sludge.

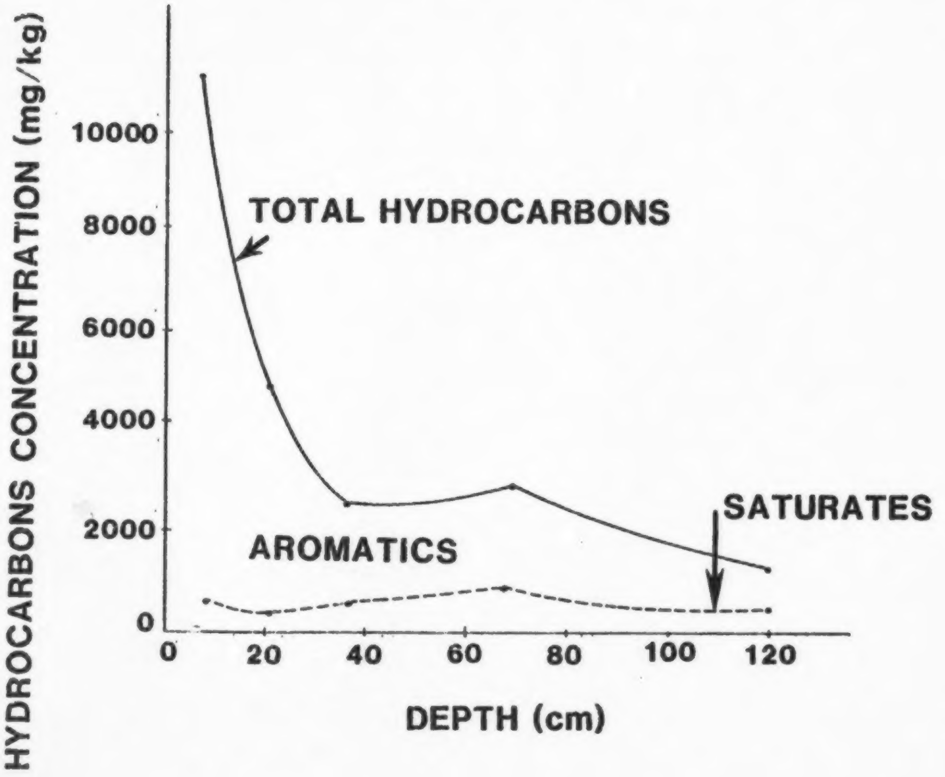


Figure 58. Distribution of hydrocarbons with depth for Lakeland soil amended with petrochemical sludge.

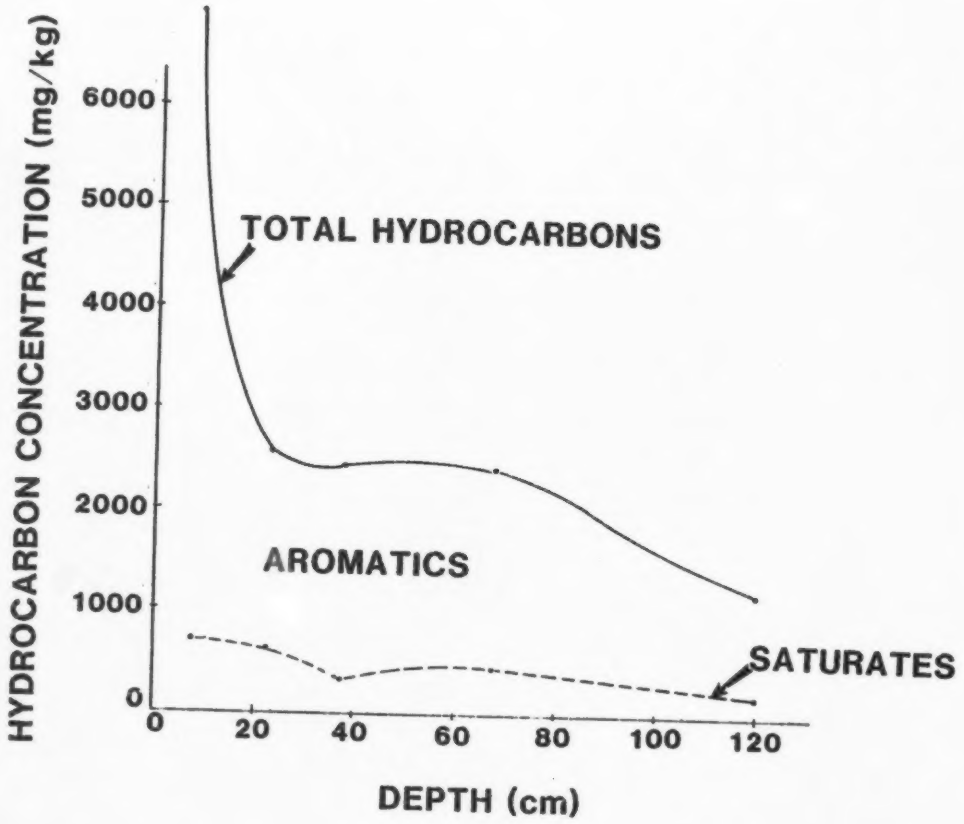


Figure 59. Distribution of hydrocarbons with depth for Norwood soil amended with petrochemical sludge.

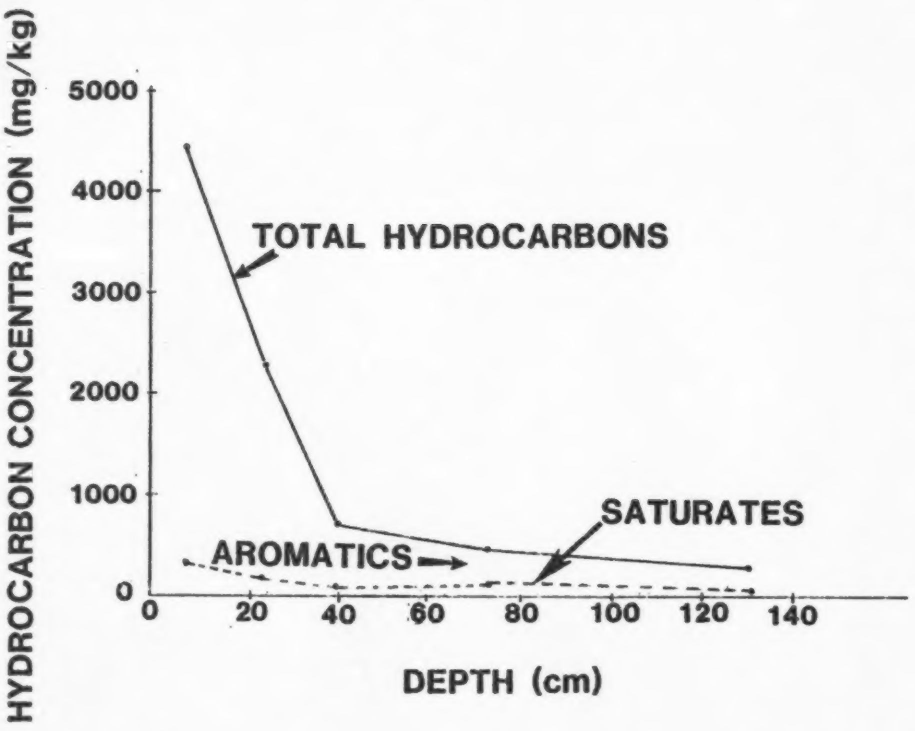


Figure 60. Distribution of hydrocarbons with depth for Bastrop soil amended with petrochemical sludge.

61A, 61B and 62C). Seemingly high saturate levels chromatographed as both peaks and conical envelope for the 7-18-81 surface sample are attributed to the errant refinery sludge loading. Its persistence is attributed to an exhausted nitrogen supply. Aromatics chromatographed for combined Fractions 2 and 3 for the Bastrop soil better describe the distribution of the petrochemical sludge with the depth and time (Figures 62A, 62B and 62C). Chromatographic profiles developed demonstrate an enhanced migration potential over the winter months. The significant portion of the aromatics recovered in the surface profile on 7-18-81 parallels the observation for the saturate fraction. Nutrients leached from the surface were sufficient to degrade the materials migrated to deeper depths.

Similar trends are demonstrated for the combined aromatic Fractions 2 and 3 of the Nacogdoches (Figure 63A and 63B) and Lakeland soils (Figure 64A and 64B). Profiles developed for Nacogdoches and Lakeland soils differ mainly from the Bastrop relative to the quantites migrated and the depth of penetration. Surface hydrocarbons were significantly dissipated in the Nacogdoches by the March 26, 1980 sampling date following the October, 1979 application of petrochemical sludge, although some remained in the lower profile. Greater quantities were observed at all depths in the Lakeland soil. Penetration of hydrocarbons chromatographed as a conical envelope was noted for the Lakeland soil to the lowest depth sampled following the second application and weathering over the winter months.

Although profiles are not shown, significant hydrocarbons were recovered in Fractions 2 and 3 of the Norwood surface horizon sampled July 16, 1981.

Withholding nitrogen fertilizer resulted in a significant carry over in surface horizons for soils receiving a 5% petrochemical sludge application. Although dissipation rates are lowered for materials migrated to deeper depths, hydrocarbons are degraded over time. A typical plot of the total hydrocarbons chromatographed with respect to time and depth is given in Figure 65 for the Bastrop soil. Arrows denote the application intervals for the 5% petrochemical sludge loading.

Summary of Soil-Water Interactions

Degradation rates for neither refinery nor petrochemical wastes were measurably influenced by soil pH or cationic distribution.

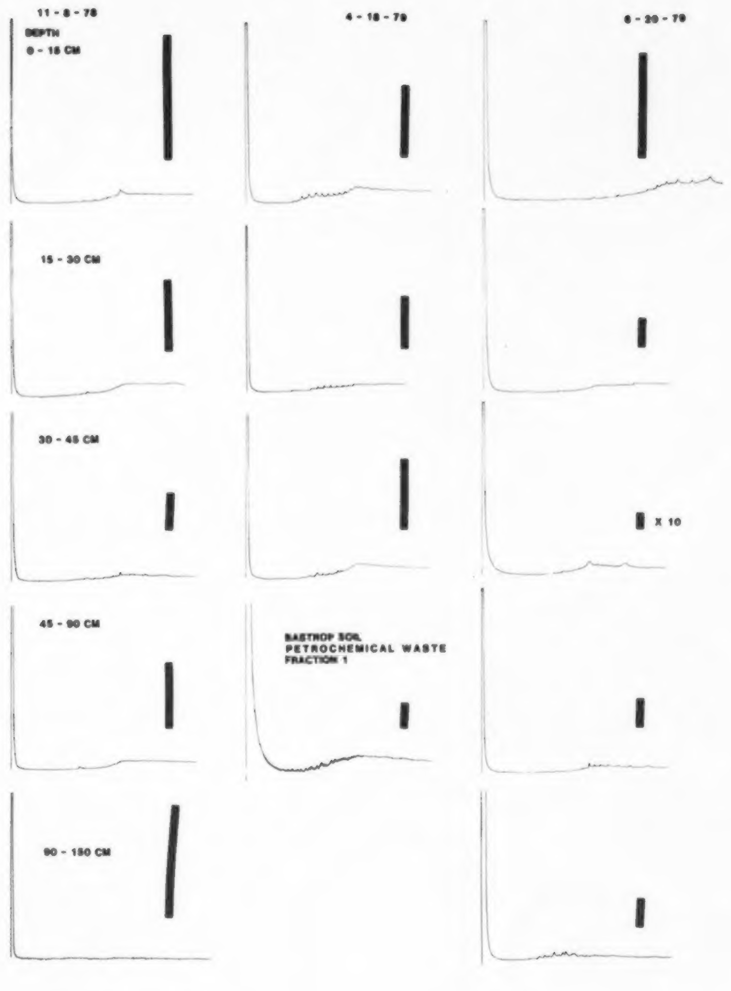


Figure 61a. GLC profile of Fraction 1 with depth and time from Bastrop soil treated with petrochemical sludge.

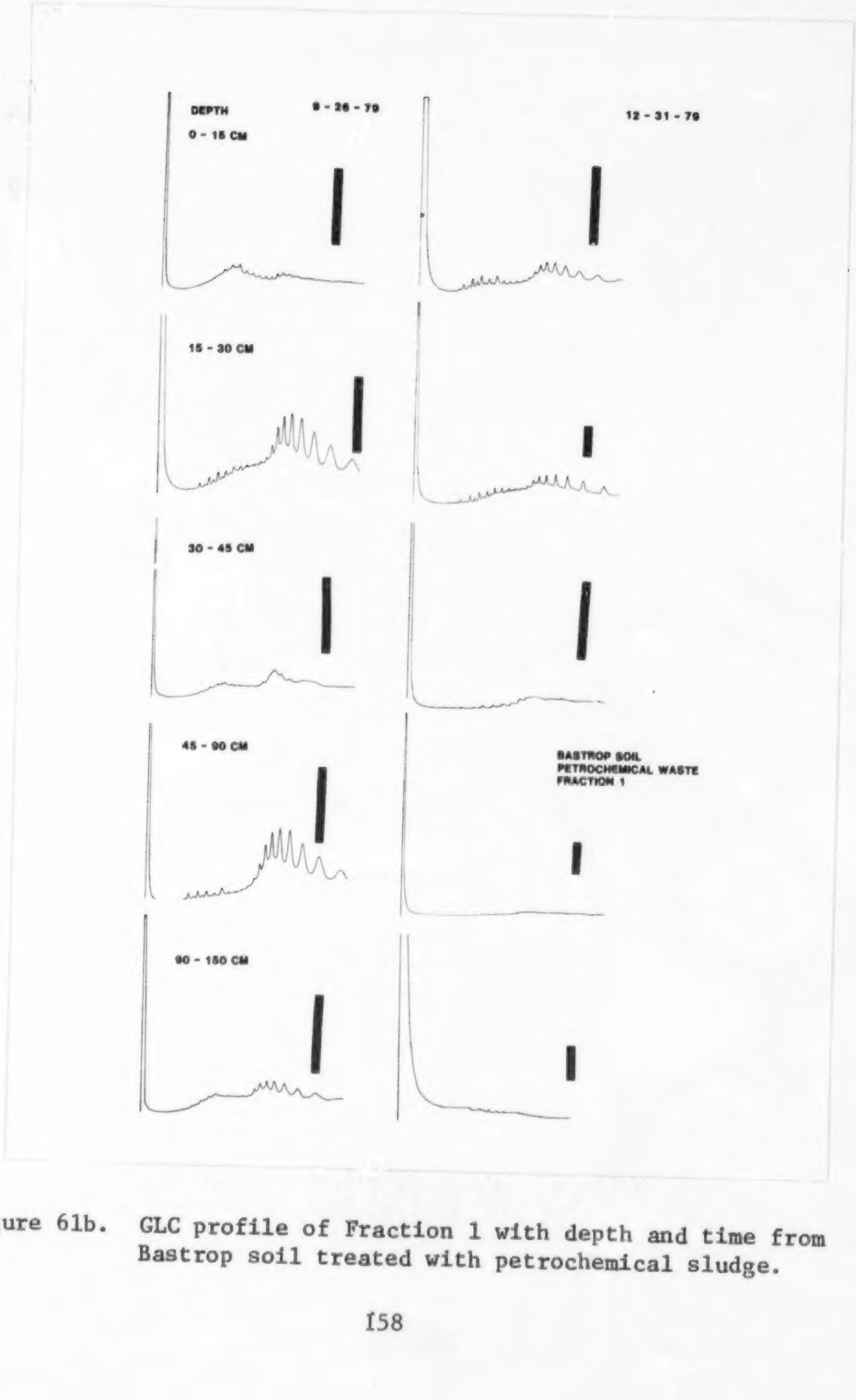


Figure 61b. GLC profile of Fraction 1 with depth and time from Bastrop soil treated with petrochemical sludge.

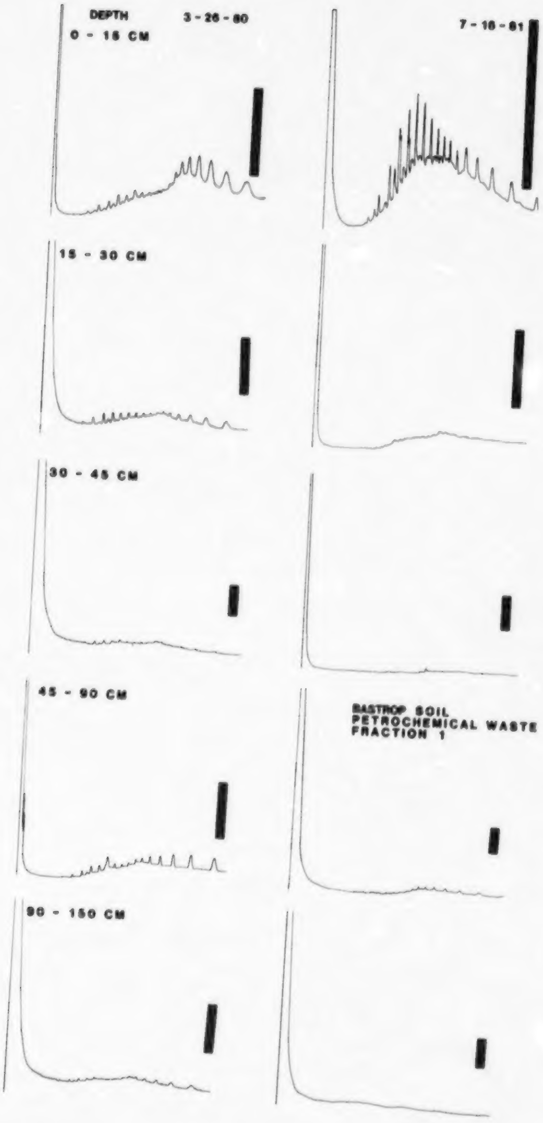


Figure 61c. GLC profile of Fraction 1 with depth and time from Bastrop soil treated with petrochemical sludge.

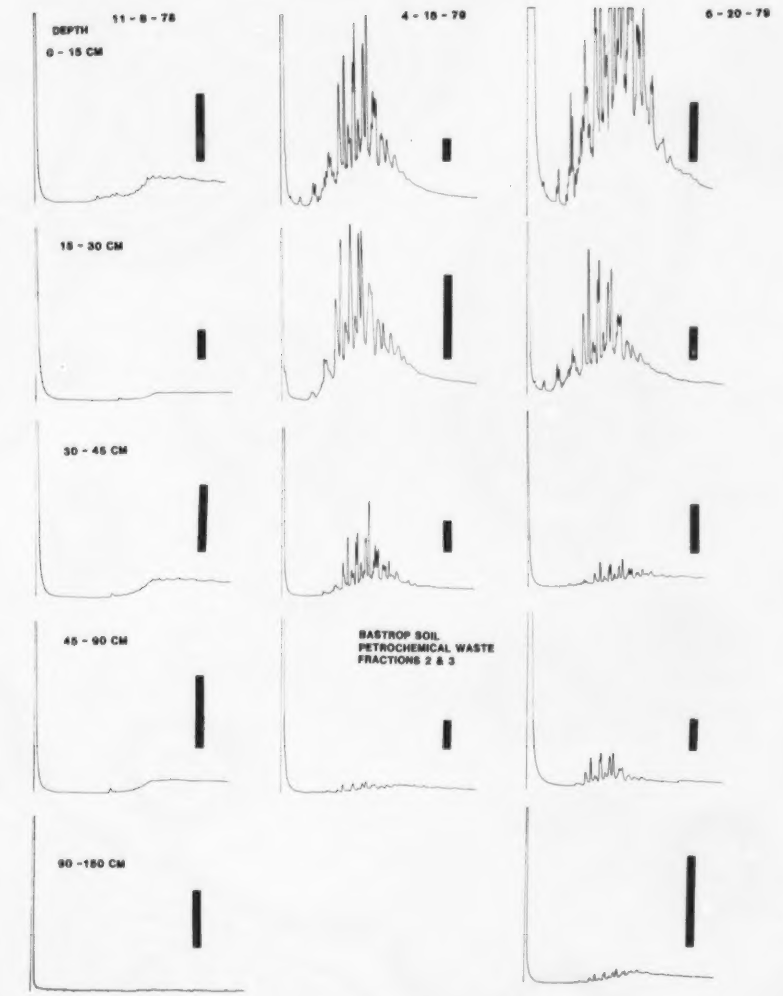


Figure 62a. GLC profile of Fractions 2 and 3 with depth and time from Bastrop soil treated with petrochemical sludge.

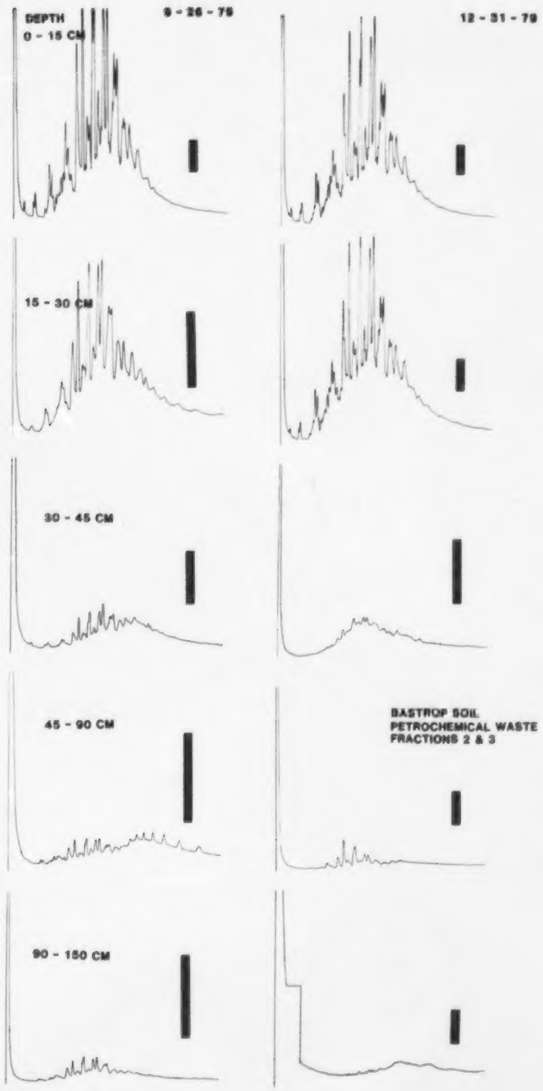


Figure 62b. GLC profile of Fractions 2 and 3 with depth and time from Bastrop soil treated with petrochemical sludge.

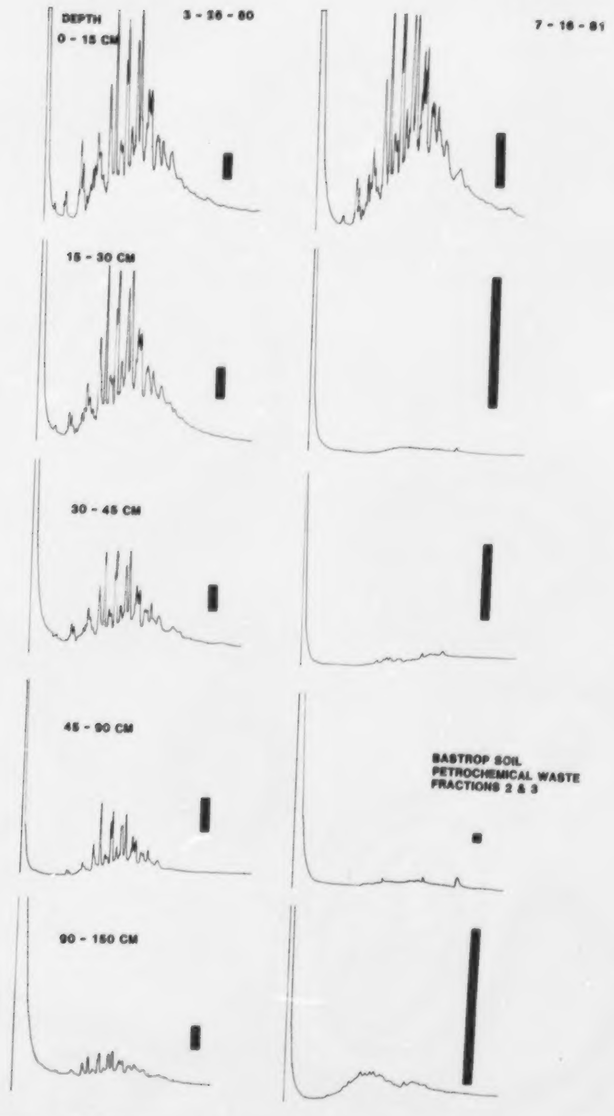


Figure 62c. GLC profile of Fractions 2 and 3 with depth and time from Bastrop soil treated with petrochemical sludge.

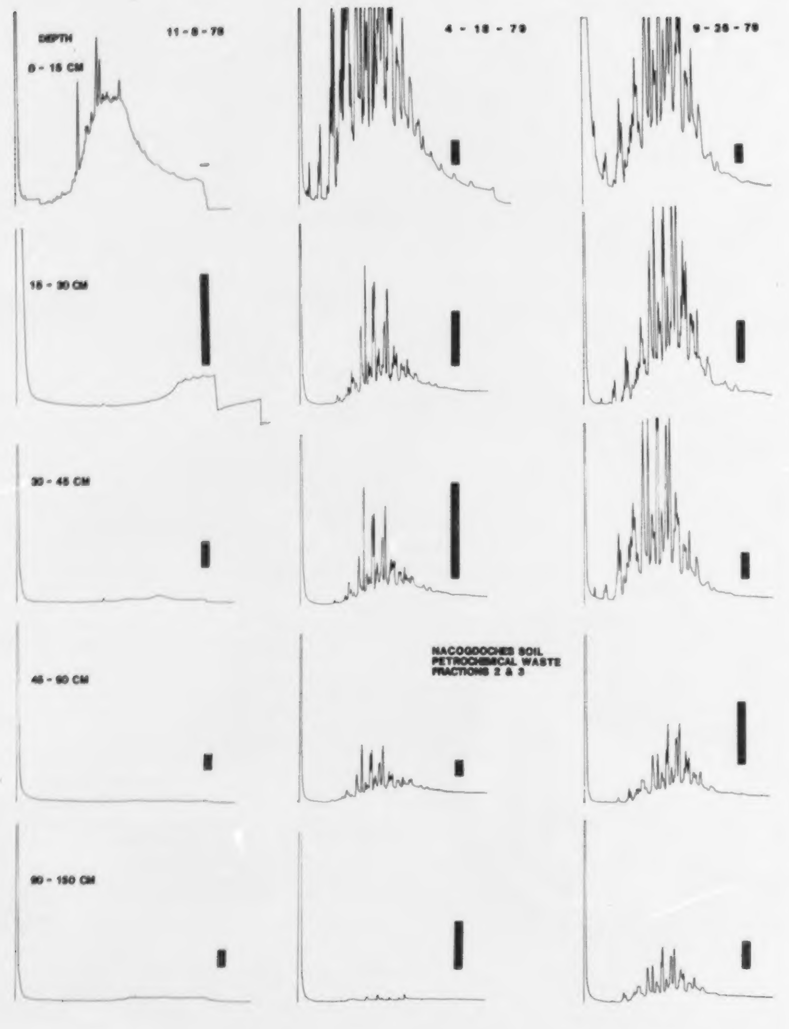


Figure 63a. GLC profile of Fractions 2 and 3 with depth and time from Nacogdoches soil treated with petrochemical sludge.

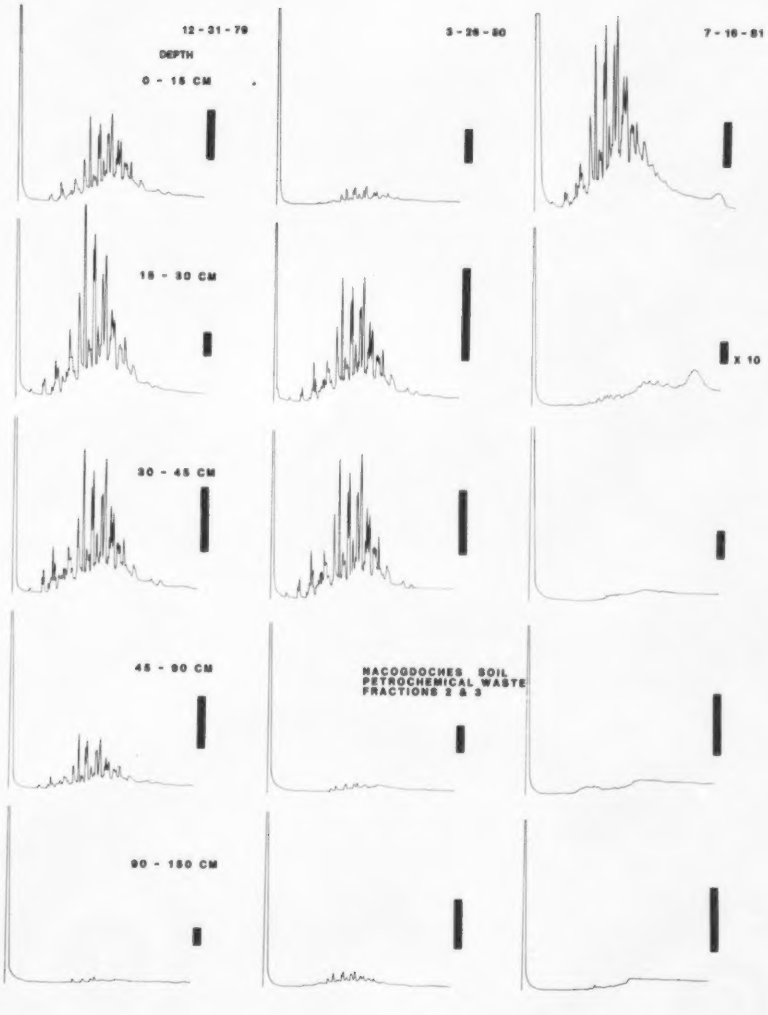


Figure 63b. GLC profile of Fractions 2 and 3 with depth and time from Nacogdoches soil treated with petrochemical sludge.

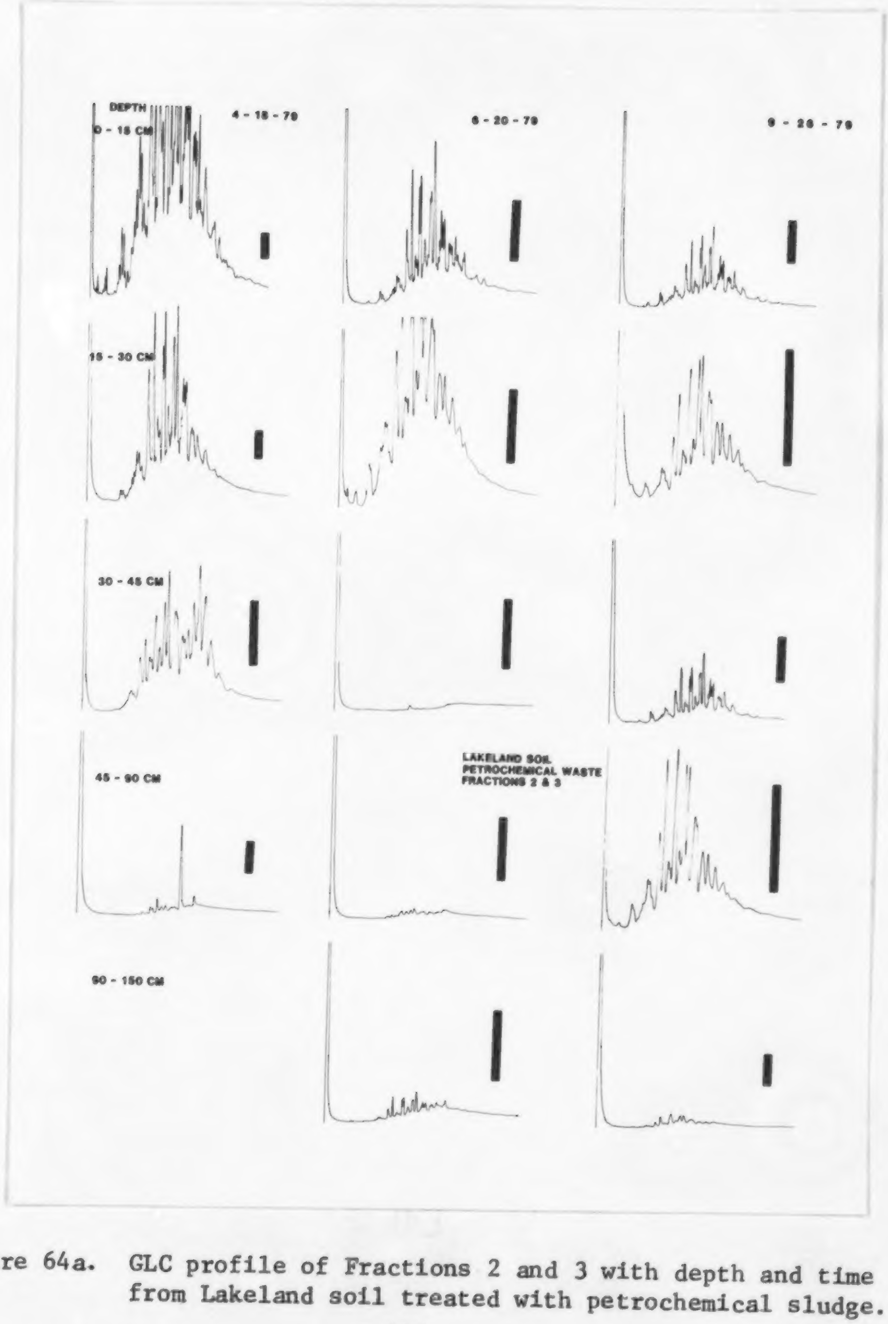


Figure 64a. GLC profile of Fractions 2 and 3 with depth and time from Lakeland soil treated with petrochemical sludge.

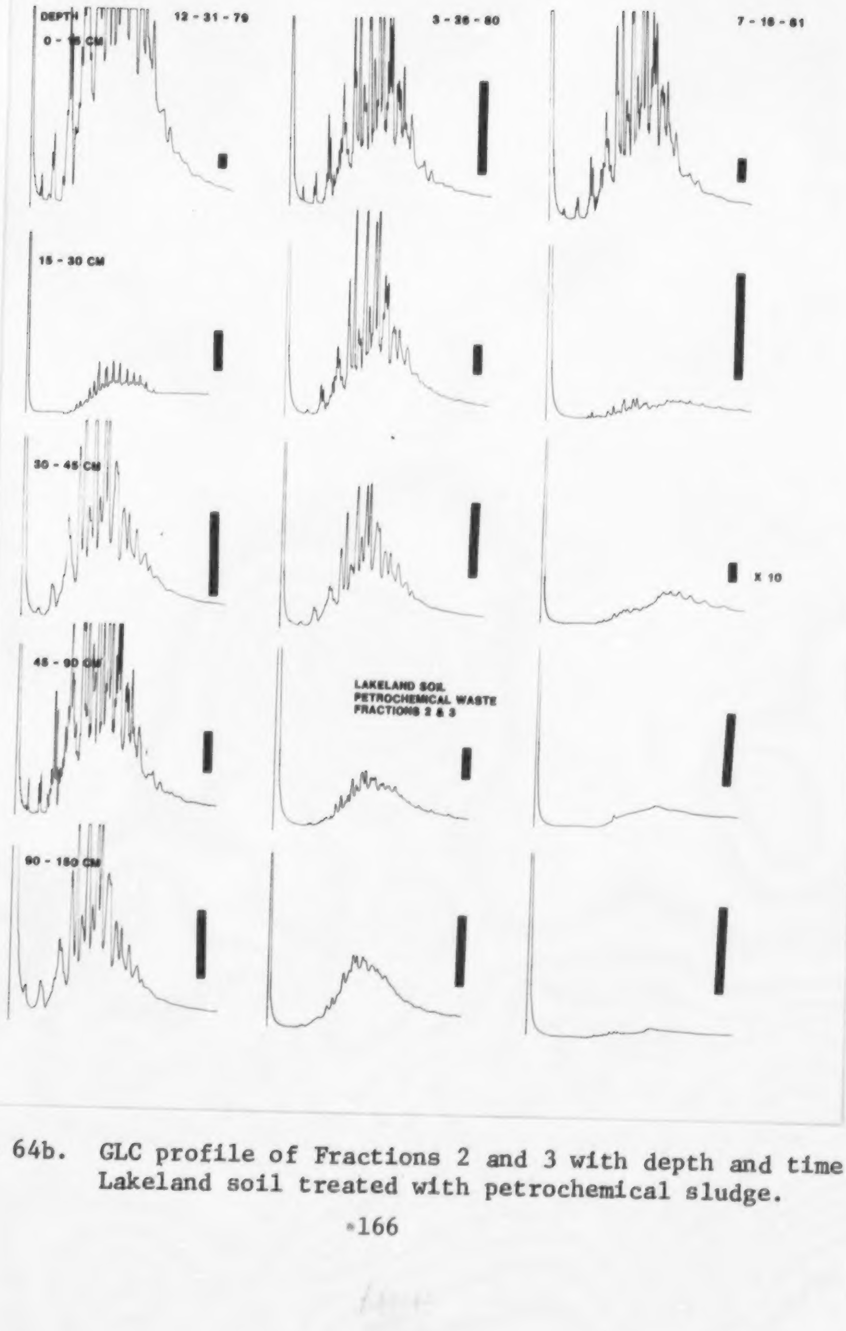


Figure 64b. GLC profile of Fractions 2 and 3 with depth and time from Lakeland soil treated with petrochemical sludge.

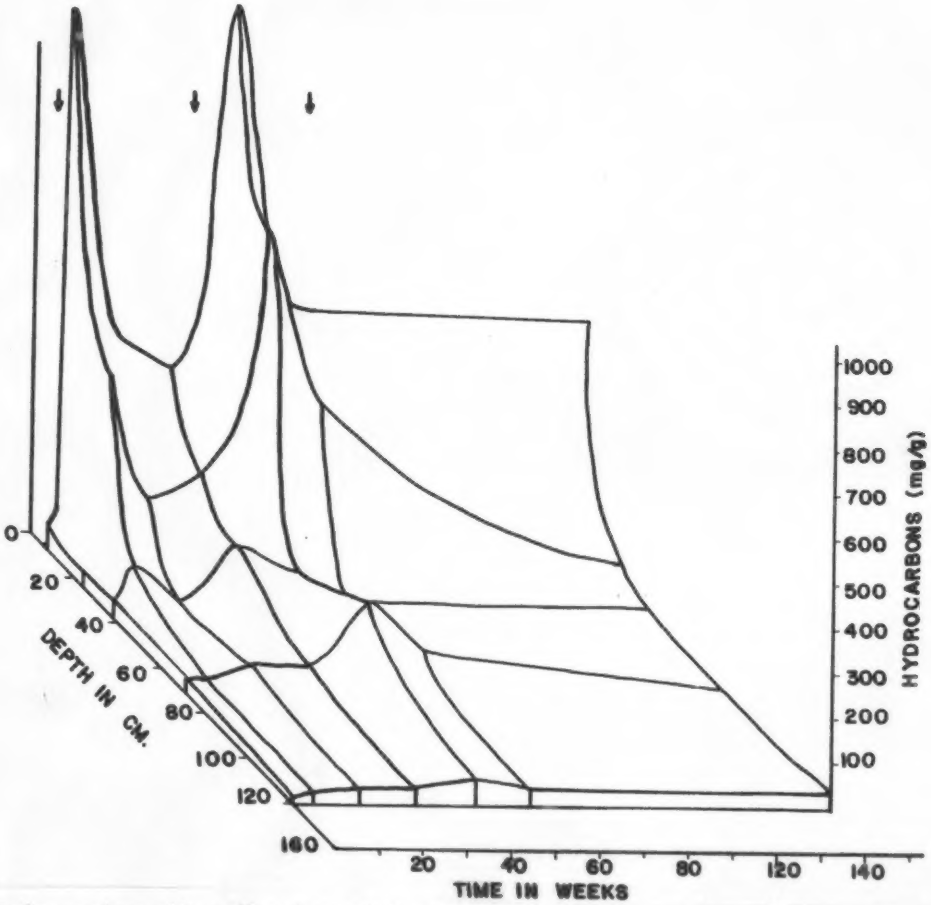


Figure 65. Hydrocarbon distribution with respect to time and depth for a Bastrop soil amended with petrochemical sludge.

Soil texture had a profound effect on the depth of migration. Depth of penetration was inversely related to the degradation rates observed when fertility was not a limiting factor. The deeper the depth of migration, the slower it decomposed. Withholding nitrogen fertilizer reversed the trend and retarded decomposition in the zone of incorporation. This observation is an anomaly attributed to nutrients leached from the surface profile, and the attendant nutritive requirements related to the material balance within a given depth interval. Hydrocarbon levels within surface horizons were materially greater than subsurface horizons requiring a greater nutritive level.

Climatic factors were normalized over soils because of the juxtaposition of the field installed lysimeters. Degradation rates were diminished for both refinery and petrochemical waste sludges over the winter months corresponding to the lowered soil temperatures.

GLC analysis in combination with column chromatographic technique was demonstrated as an effective means of monitoring the fate of complex waste hydrocarbons applied to soils.

Leachate Volumes

Graphs showing the cumulative amount of leachate as a function of time are presented in Figures 66 to 69. The Nacogdoches lysimeters (1-5) had the greatest amount of total leachate and ranged from 25 to 45 cm. These were followed by the Norwood lysimeters (11-15), Lakeland lysimeters (6-10) and Bastrop lysimeters (16-20). In most cases, the initial leachate collection rate beginning December 1978-January 1979 lasting until July 79 was fairly rapid due to a large moisture reserve from the previous months. Leachate collection was low July 79-Jan 80 due to limited rainfall and high evaporative demand. A general rise in the rate of leachate was observed in the beginning 6 months of 1980 again due to the resupply of moisture over winter months. Thus a noticeable cycle in leachate is evident with soil moisture accumulating in fall; leaching in Jan-July; little leaching from August-December due to high summer evaporative demand and the initial fall rains being needed to restore the moisture reserve and thus repeat the cycle.

These data show that significant amounts of water moved through all the soil profiles during the period under investigation. Natural rainfall was relied on to allow a normal moisture regime so that the data would be as

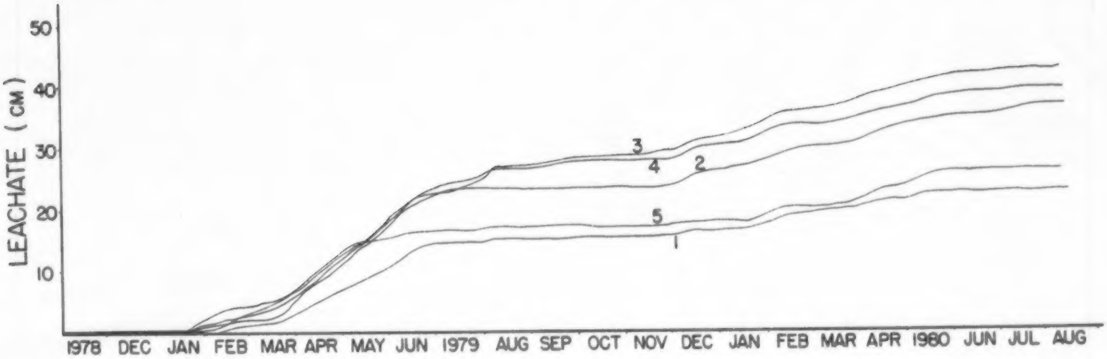


Figure 66. Cumulative leachate from the Nacogdoches soil lysimeters.

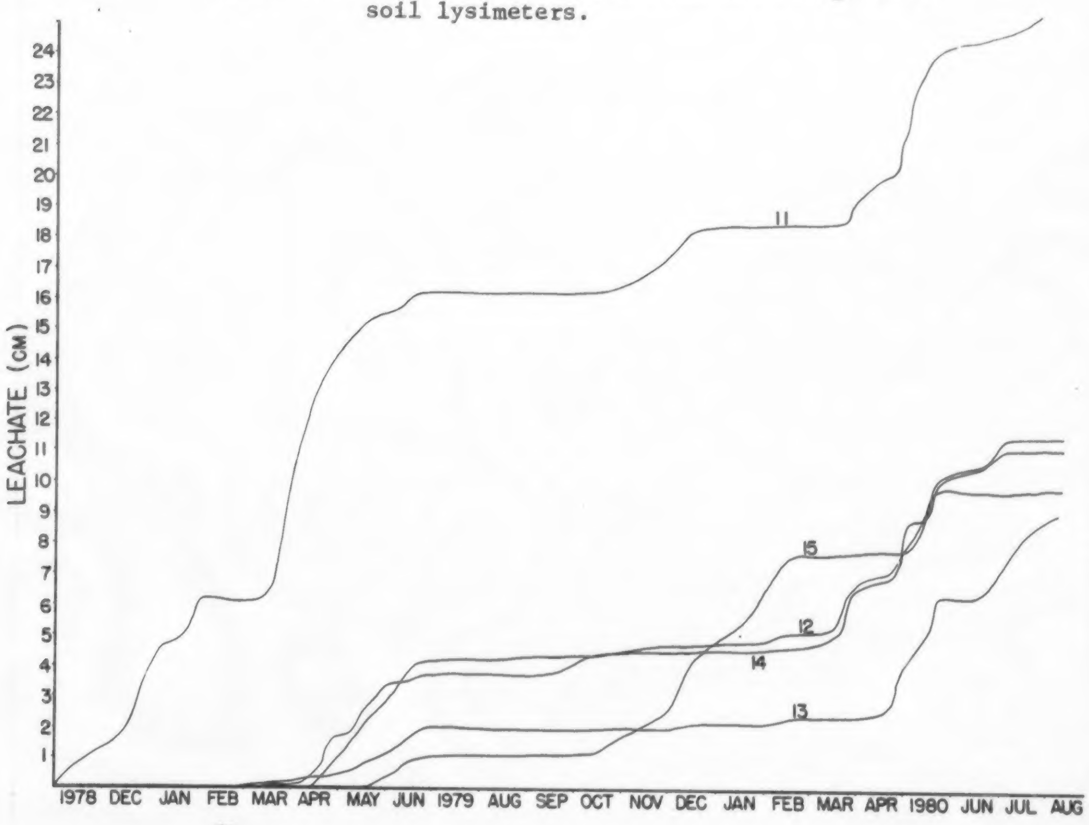


Figure 67. Cumulative leachate from the Norwood soil lysimeters.

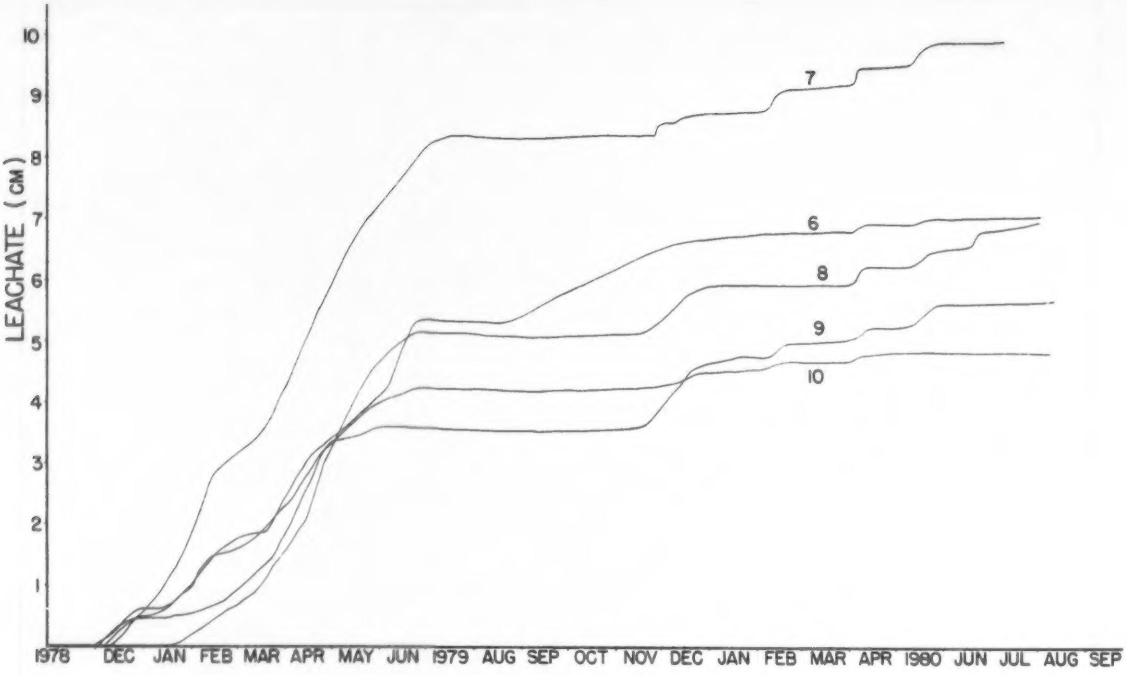


Figure 68. Cumulative leachate from the Lakeland soil lysimeters.

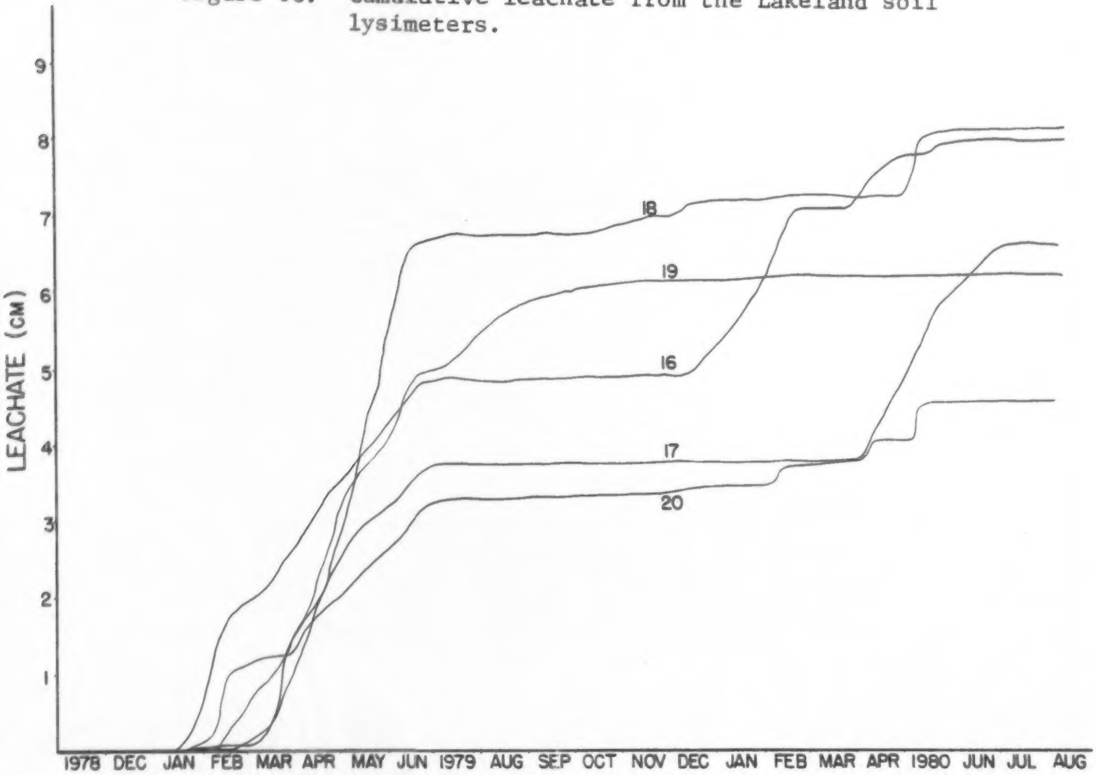


Figure 69. Cumulative leachate from the Bastrop soil lysimeters.

representative as possible of actual field conditions. The leachate volumes were not sufficient to displace a full pore volume from any of the profiles during the period of investigation.

Leachate Samples

Leachate samples from the Nacogdoches soils before sludge applications were free of hydrocarbons and gave a very nearly flat chromatograph. The two very small peaks which occur on either side of the center of the chromatograph appear in extracts of many samples, including those collected before any waste was applied. They are thus assumed to be the result of naturally occuring contaminants or contaminants picked up from the plastic collection tubes.

Leachate from lysimeter 1 which received only one application of refinery sludge remained clean throughout the study period. Typical chromatograms of the leachate collected before and after refinery sludge application are given in Figure 70. Leachate from lysimeter 2 which also contained Nacogdoches soil, but received 3 applications of refinery sludge, remained free of hydrocarbons throughout the study period. Chromatograms of leachate from this lysimeter were similar to those in Figure 70 and therefore are not presented.

Leachate samples from lysimeters 3 and 4 containing Nacogdoches soil and receiving 3 and 1 applications, respectively, of petrochemical sludge showed a similar lack of hydrocarbons. Figure 71 shows typical pre and post petrochemical sludge application chromatograms, and there is no evidence of any leachate contamination.

Leachates from lysimeters of Lakeland, deep sandy soil, also were free of hydrocarbons. Typical chromatograms of leachate before application and after 2 applications of refinery sludge are shown in Figure 72. Lysimeter 7 also received 2 applications of refinery sludge and had leachate free of hydrocarbons. Background leachate samples from lysimeters 8 and 9 before application of petrochemical sludge were unable to be obtained due to dry soil conditions. Therefore the leachate analyses were compared to leachate samples from the control Lakeland lysimeter #10. Figure 73 contains chromatograms of the control lysimeter and lysimeter 9 which received 1 application of petrochemical sludge. Both chromatograms show only 1 small peak probably a result of a naturally occuring compound in the soil or a low concentration of a contaminant from the leachate collection system. Leachate from lysimeter #8

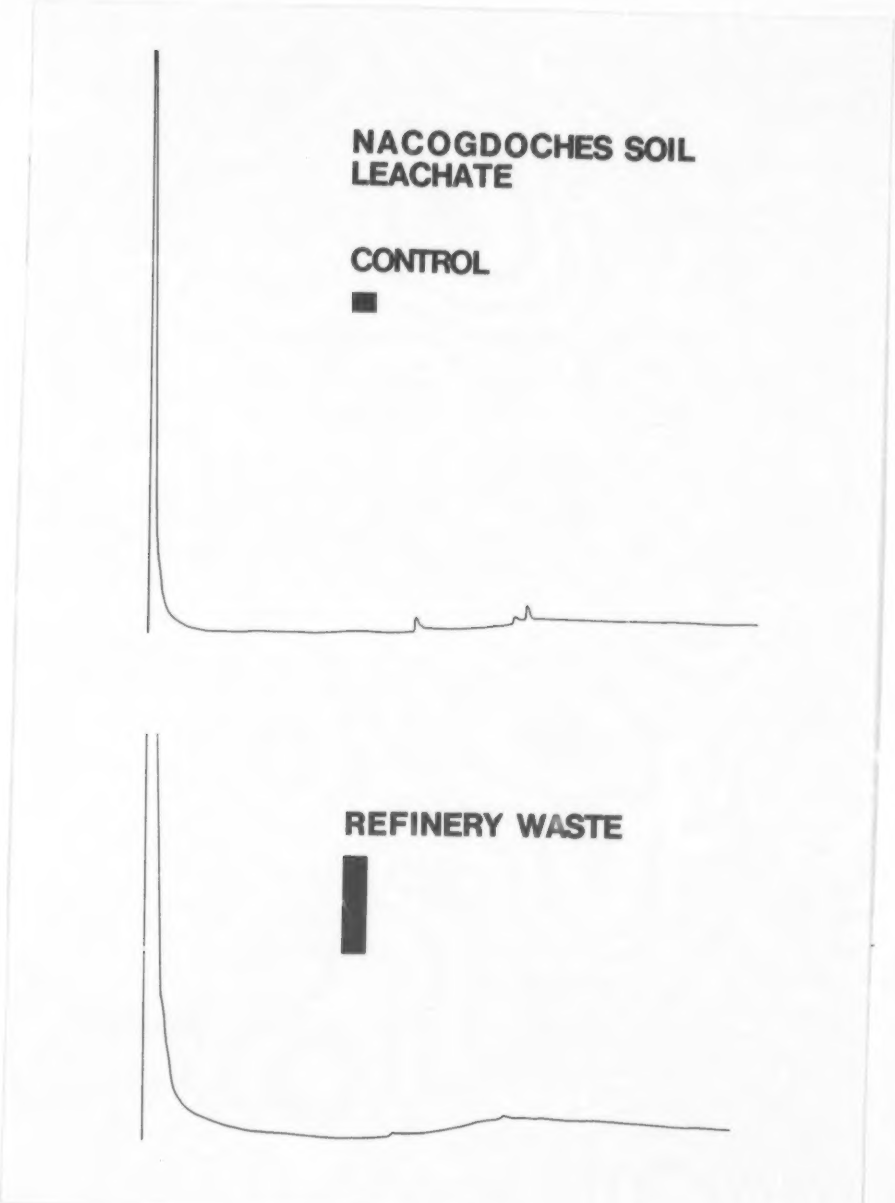


Figure 70. Chromatograms of leachate from Nacogdoches soil before and 51 weeks after one application of refinery waste.

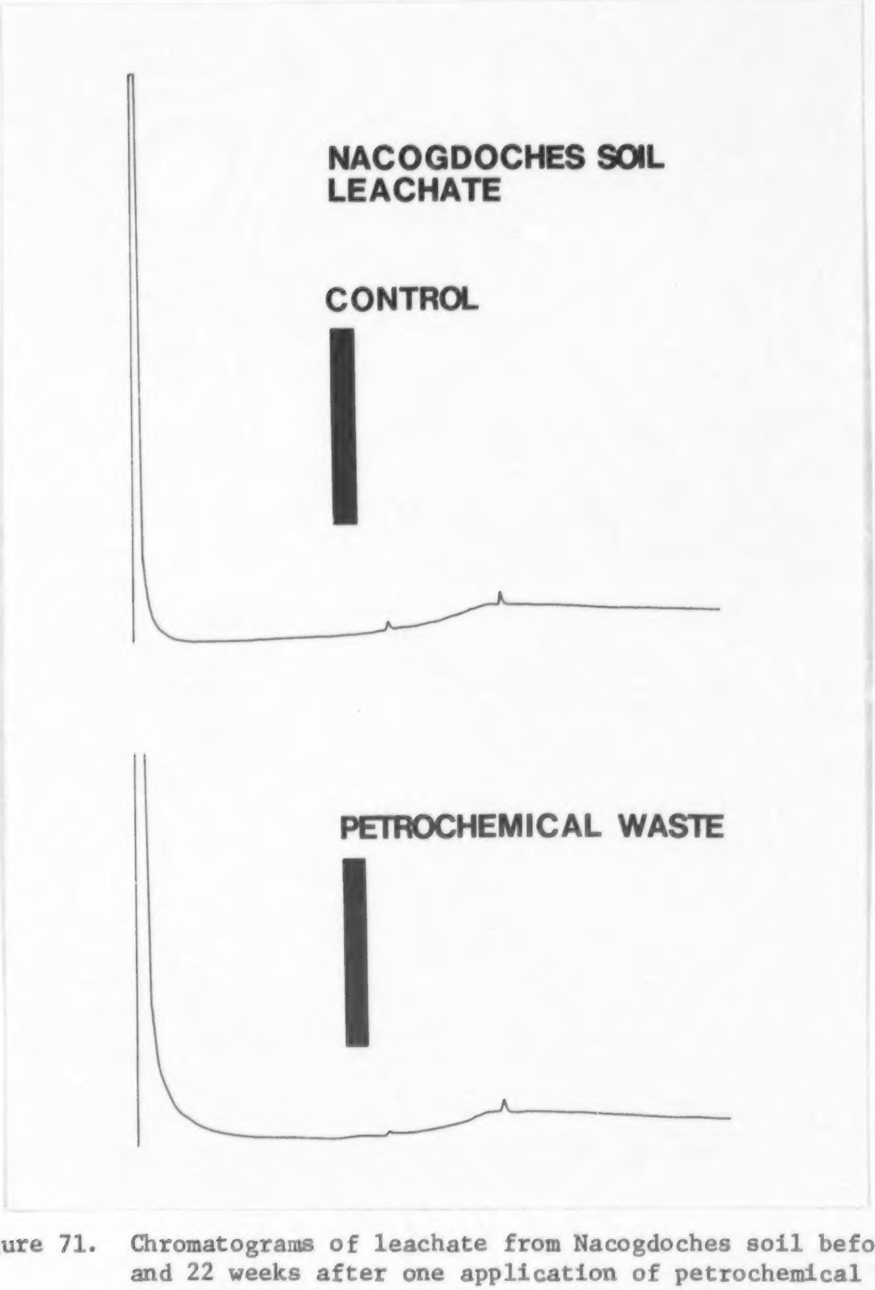


Figure 71. Chromatograms of leachate from Nacogdoches soil before and 22 weeks after one application of petrochemical waste.

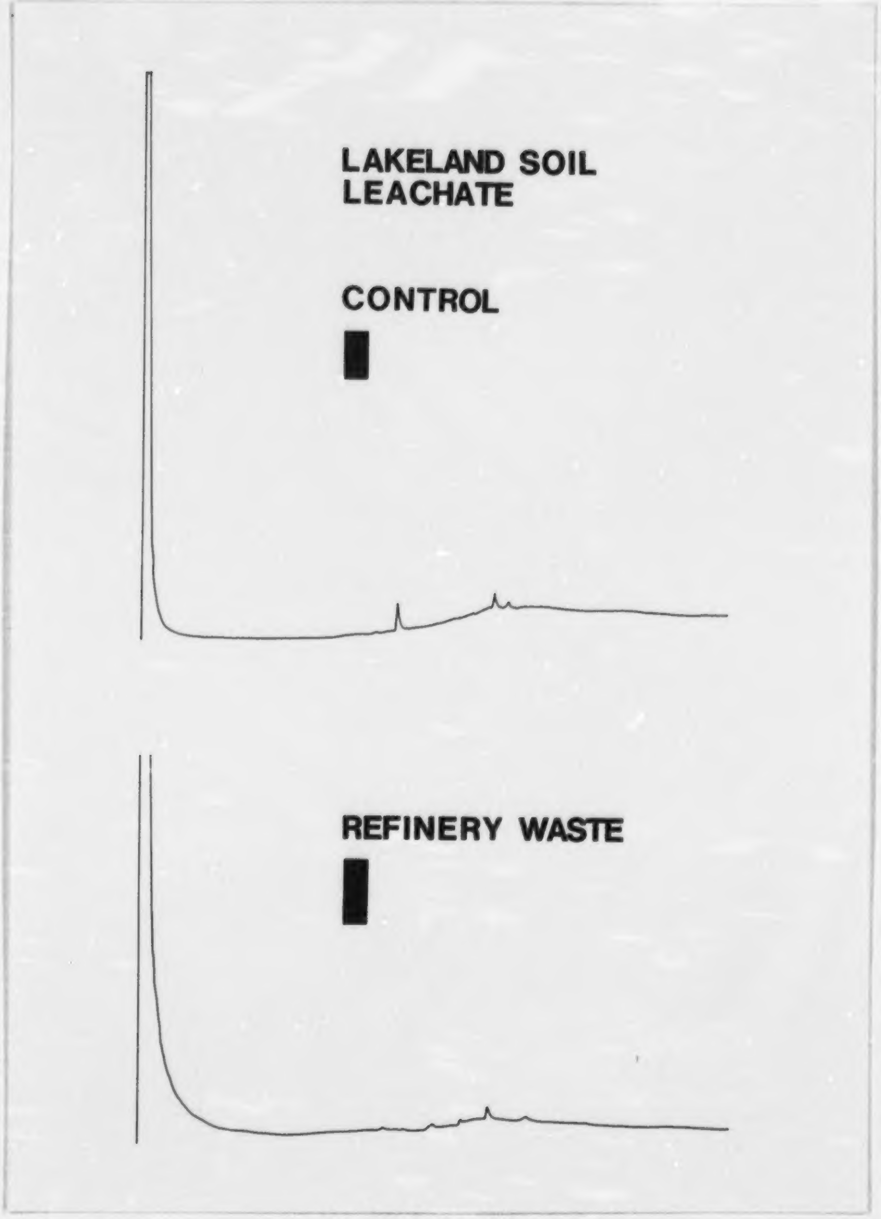


Figure 72. Chromatograms of leachate from Lakeland soil before and 18 weeks after second application of refinery waste.

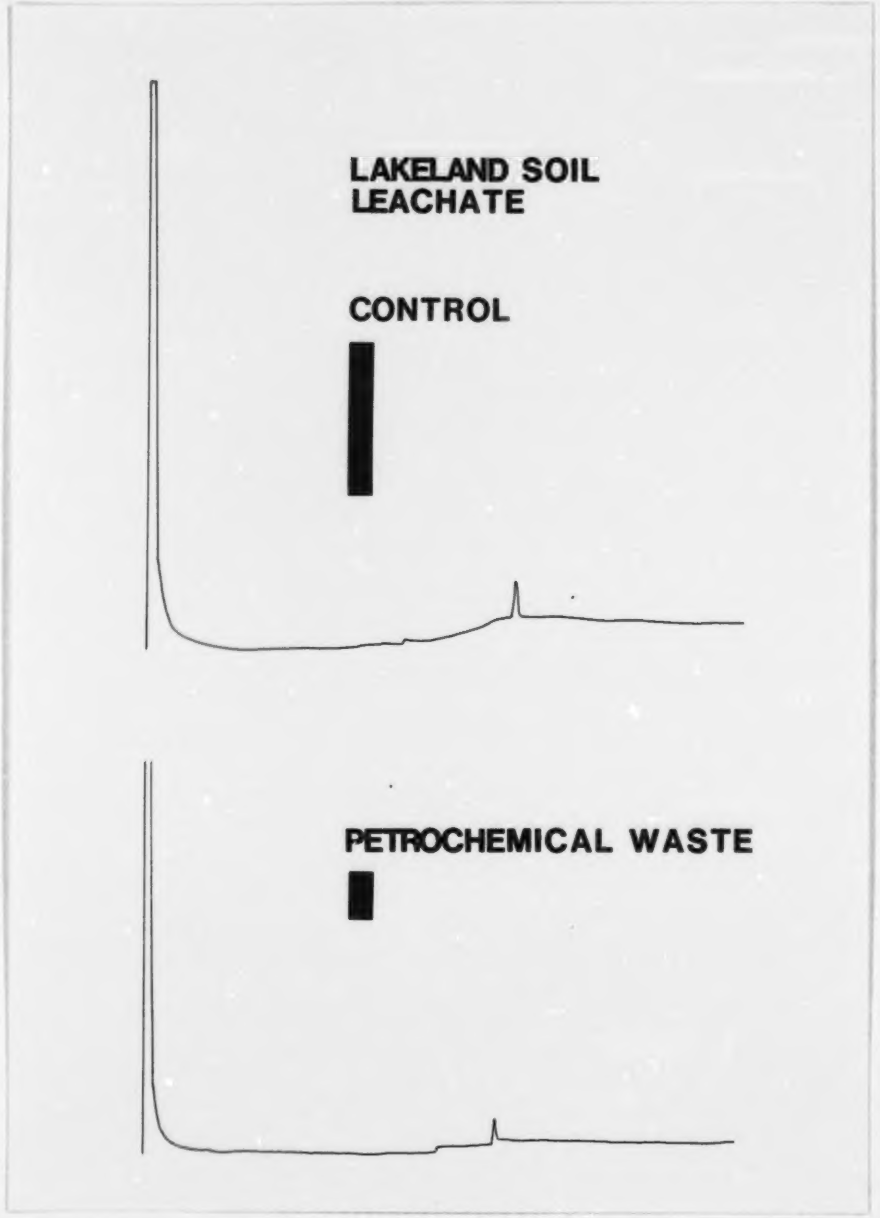


Figure 73. Chromatograms of leachate from Lakeland soil before and 14 weeks after one application of petrochemical waste.

which received 3 petrochemical sludge applications, likewise, was free of hydrocarbons.

All leachate samples from before and after one application of refinery waste to Norwood soil in lysimeter #11 were free of any hydrocarbons. Lysimeter 12, also containing Norwood soil, received 2 applications of refinery waste. Figure 74 shows typical chromatograms of before and after leachate samples which were free of hydrocarbons.

Leachate from lysimeter #13 which contained Norwood soil and received 3 applications of petrochemical sludge, was free of hydrocarbons (Figure 75). Likewise lysimeter 14 which received 1 application each of refinery and petrochemical sludge showed no hydrocarbons in the leachate. Figure 75 shows only one noteworthy peak which is probably a comtaminant and was not identified.

Lysimeters 16 and 18 each contained Bastrop soil and received 2 and 1 applications respectively of refinery sludge. Typical chromatograms before application and after 2 applications are shown in Figure 76. From these data, there is no evidence of hydrocarbon contamination of the leachate.

Lysimeter 17 containing Bastrop soil received 3 applications of petrochemical sludge. A typical background chromatogram and chromatogram of leachate after three applications is shown in Figure 77. No hydrocarbons were identified in the leachate. Lysimeter 19 received one application of petrochemical sludge followed by an application of refinery sludge. Leachate from this lysimeter was similar to the others and was free of hydrocarbons. Therefore, individual data are not presented.

Hydrocarbons were not found in detectable concentrations in the leachate from the control lysimeters, nor from those that had received applications of either the refinery or petrochemical wastes. The leachate collected as long as 2 years after waste application remained free of hydrocarbons.

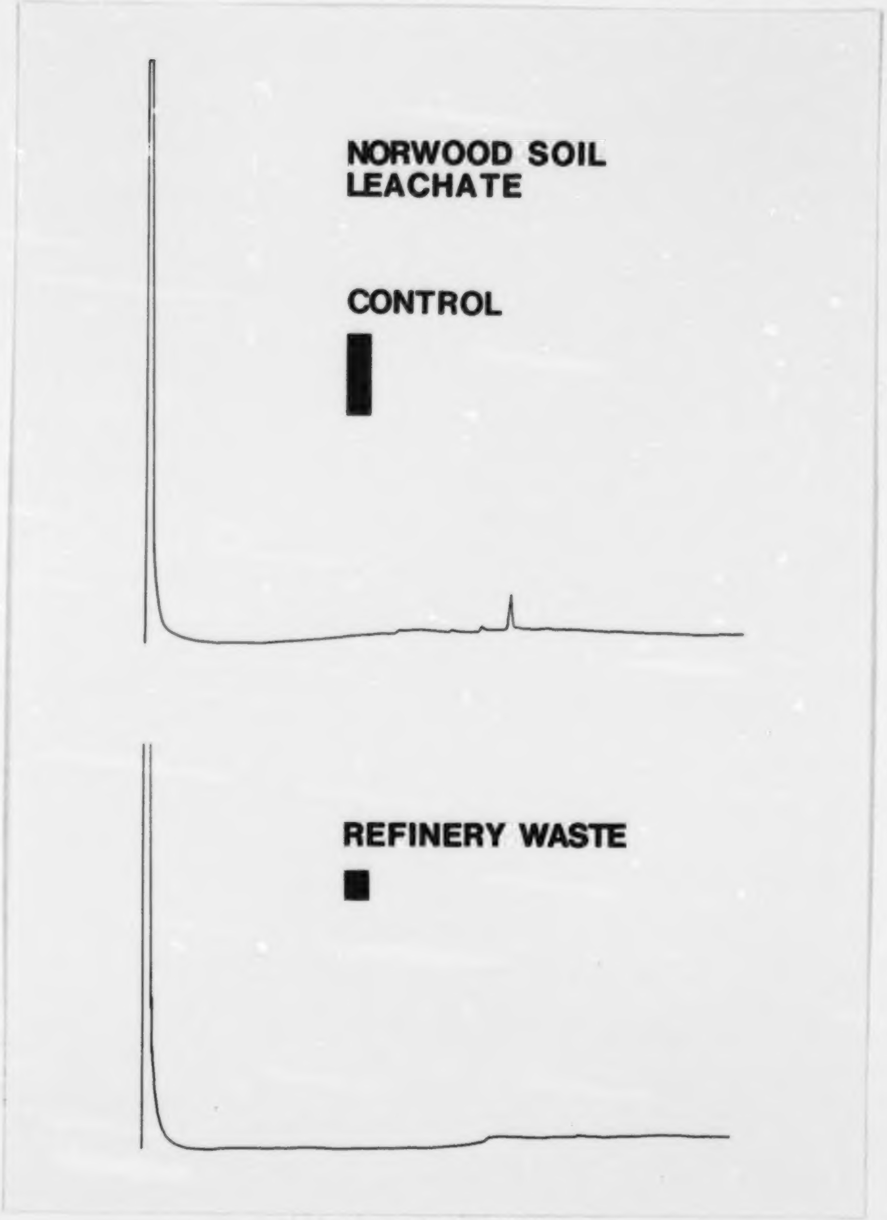


Table 74. Chromatograms of leachate from Norwood soil before and 29 weeks after second application of refinery waste.

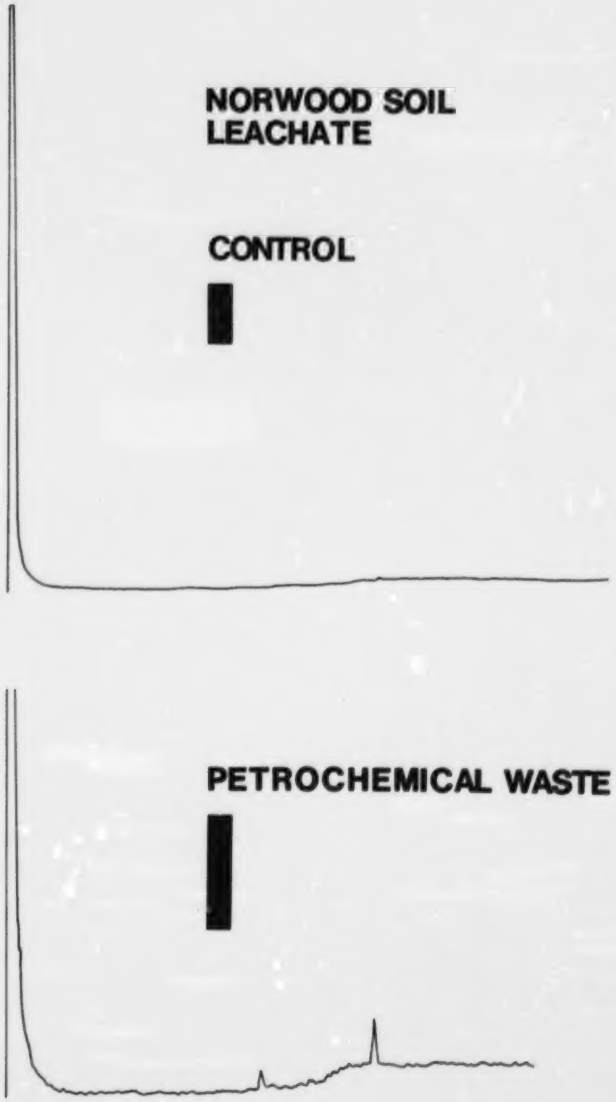


Figure 75. Chromatograms of leachate from Norwood soil before and 10 weeks after third application of petrochemical waste.

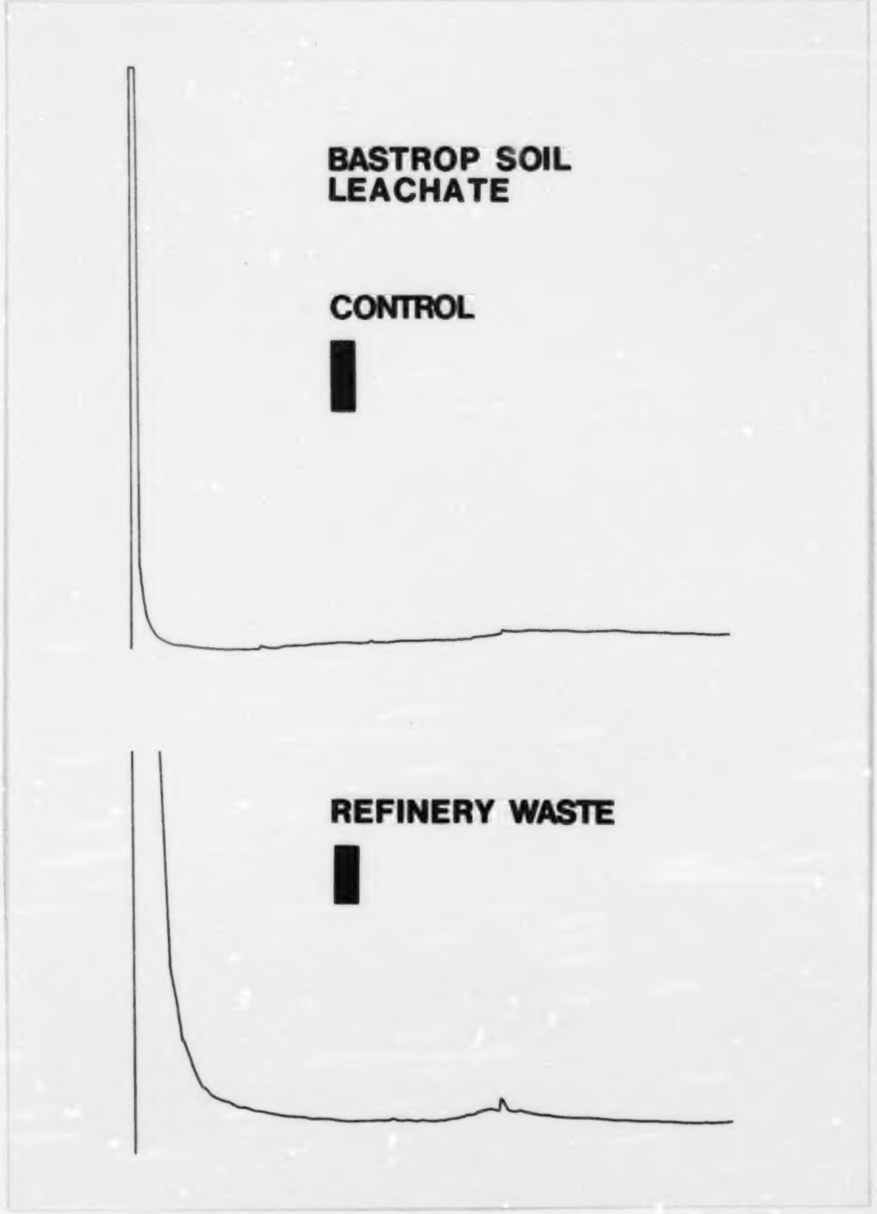


Figure 76. Chromatograms of leachate from Bastrop soil before and 39 weeks after second application of refinery waste.

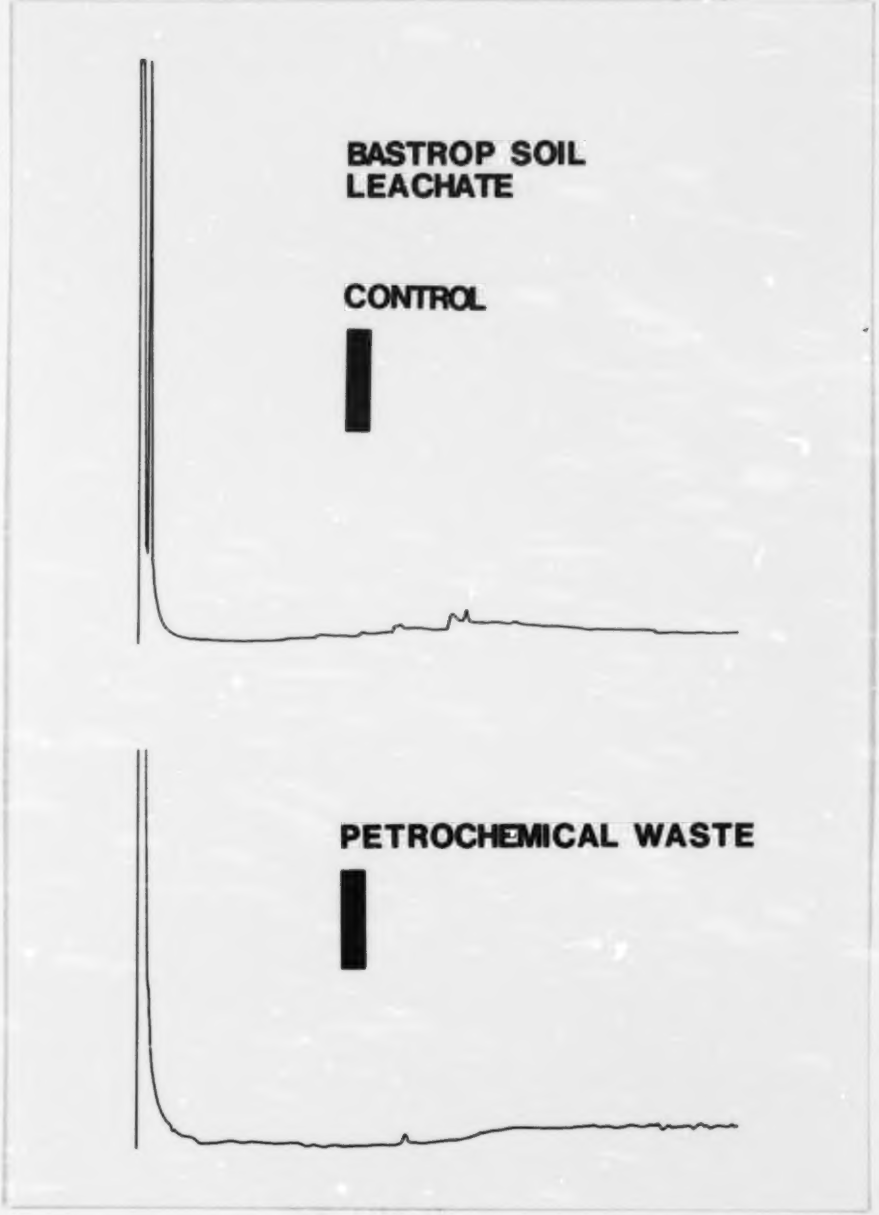


Figure 77. Chromatograms of leachate from Bastrop soil before and 10 weeks after third application of petrochemical waste.

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